Halogen Lamp Design & Manufacturing

by David R. Dayton

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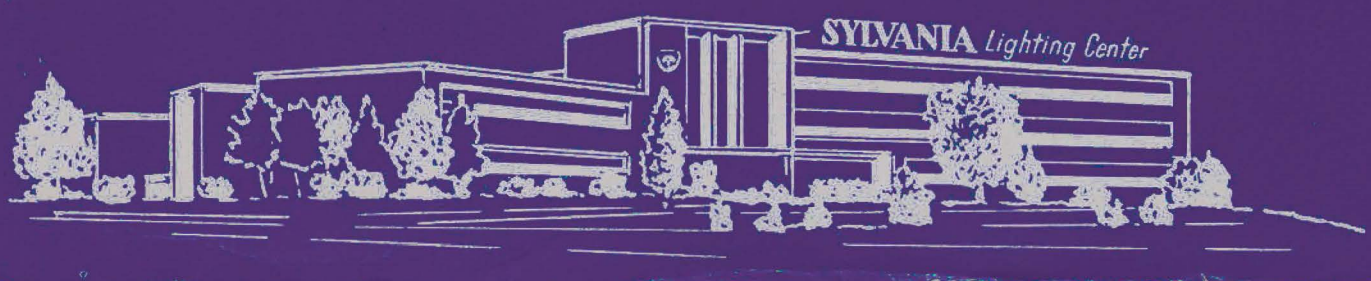

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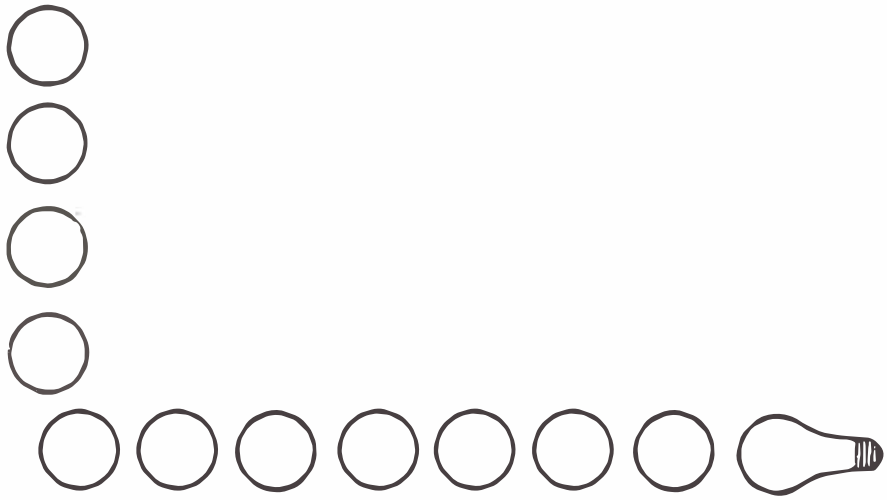

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1.0 THE HALOGEN CYCLE

For a proper understanding of the value of the Halogen Cycle, it is necessary to take a close look at the process by which the light output of a conventional lamp deteriorates during lamp life.

1.1 Lumen Maintenance of Incandescent Lamps

1.1.1 Vacuum Lamps

The tungsten filament evaporates during lamp operation. The tungsten vapor condenses on the glass bulb. The process continues throughout lamp life and the light output decreases accordingly. The loss in light output can be diminished by using larger bulbs. The larger the bulb, the less dense the tungsten deposit and the greater lumen maintenance. Bulbs are usually sized such that lumen maintenance will be greater than 70% at 70% of rated life.

1.1.2 Gas Filled Lamps

In a gas-filled lamp, the situation is much the same as in vacuum lamps. The only difference is that due to the convection currents in a gas-filled lamp, the tungsten deposits on glass surfaces above the filament instead of all over the bulb. The rate of tungsten deposit for a given filament temperature is far less, but gas-filled lamps are run at much higher efficiencies. The net result is the same and again the smaller the bulb the more the decrease in lumen maintenance. It is also true that an impure fill-gas results in accelerated lamp deterioration compared to lamps made with inert gases and clean lamp parts. Getters and good lamp making practices are used to minimize the problem. In some special studio lamps, tungsten powder is sealed into lamps which can be shaken around to "scour" off the tungsten deposits and renew the light output. The halogen cycle removes the tungsten deposits and/or keeps the tungsten from condensing and returns the tungsten to the filament. This process eliminates lossof lumens due to condensed tungsten on internal glass surfaces.

1.2 General Halogen Cycle Mechanism

The halogen cycle in its simplest form is as follows. The halogen can be iodine, bromine, chlorine or fluorine or a combination of any of the halogens.

Tungsten + halogen at room temperature → no chemical action

Tungsten + halogen at Temperature A → W (halogen)$_x$ solid

W (halogen)$_x$ solid at Temperature B → W (halogen)$_x$ vapor

W (halogen)$_x$ vapor at Temperature C → W vapor + X halogen vapor

W vapor condenses on filament and halogen remains in gas phase to start cycle with more tungsten.

The above is an over simplification because the temperatures in a typical bulb vary from minimum bulb wall temperature to filament temperature. With such a range in temperatures (close to 3000°K) and other materials present besides W, quartz and halogen, there are many reactions and reaction rates occurring simultaneously.

Figure 1.2.1 shows some of the reactions which occur in tungsten-iodine lamp.

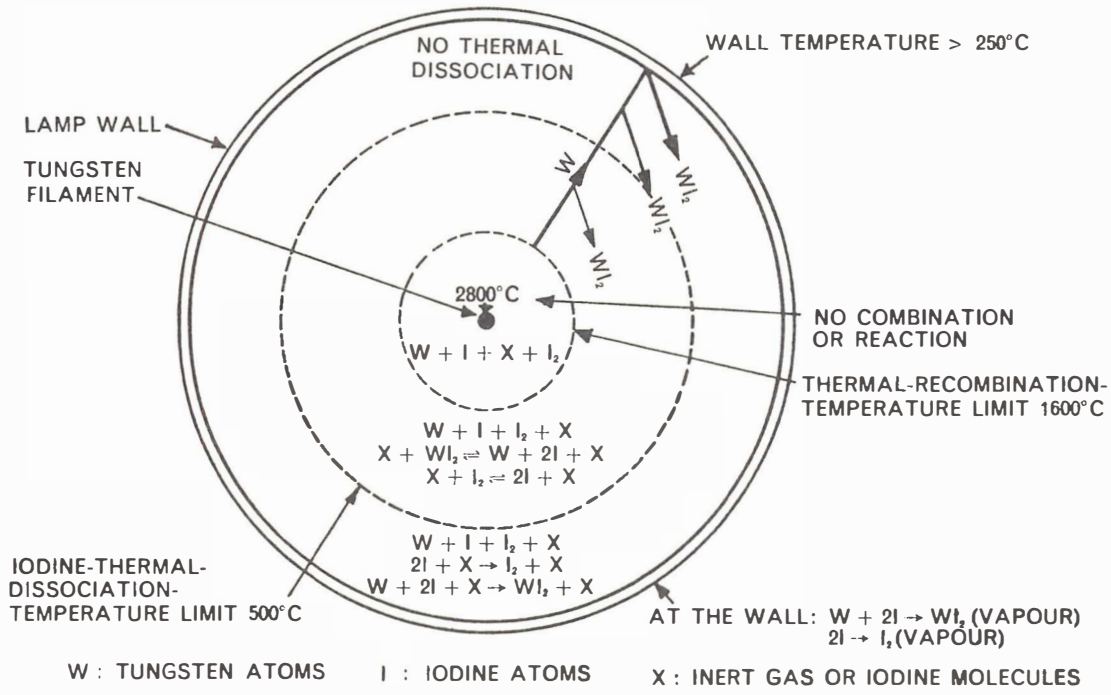


FIGURE 1.2.1

ADVANTAGES OF THE HALOGEN CYCLE

The advantages of the halogen addition is not that it prolongs the life of the lamp. There are, however, three real advantages:

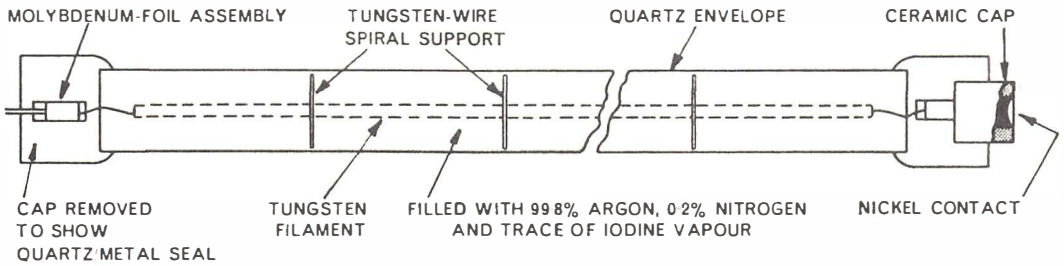
1. The bulb wall does not blacken. The efficacy therefore does not decrease during life because there is little or no absorption in the bulb wall.

2. Since the bulb wall remains clear, a very small envelope around the filament can be chosen. (Without halogen this small tube blackens rapidly, because the same amount of tungsten condenses on a small area.) This narrow envelope permits the use of a high rare-gas pressure, which results in a longer life or a higher efficacy. Because of the small size of the bulb, the bulb wall will be hot, but this is advantageous for the evaporation of the tungsten halogen compound. Because of the high temperature of the bulb wall, practically all halogen lamps are made of quartz glass, vycor or very hard glass.

3. Because of the small volume of the lamp and notwithstanding the high rare-gas pressure, the amount of rare gas in the lamp is so small, that it is economically possible to use krypton or even Xenon instead of argon, which results in a higher efficacy.

2.0 THE TUNGSTEN IODINE LAMP

2.1 Construction of a typical quartz-iodine linear lamp.



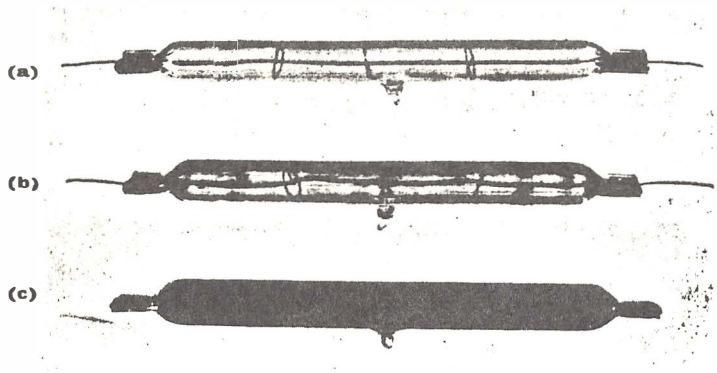
2.2 The Mechanism and Conditions for Regenerative Action

The iodine tungsten cycle is dependent upon iodine-molecular dissociation with the formation and decomposition of tungsten iodine:

$$I_2 \rightleftharpoons 2I \quad \ldots\ldots\ldots\ldots \text{(i)}.$$

$$W + 2I \rightleftharpoons WI_2 \quad \ldots\ldots\ldots\ldots \text{(ii)}.$$

In a tungsten-filament lamp containing inert gas and iodine vapor, tungsten atoms diffuse away from incandenscent filament by evaporation. Within a zone around the filament extending to a temperature in the region of 1600°C, the iodine vapor is almost completely dissociated both thermally by collision and photochemically by energy radiated from the filament. In addition, the temperature is too high for combination of tungsten and iodine atoms, which therefore behave as independent 'inert' vapors.



Early Experimental Wembley Iodine Lamp
(a) Before burning
(b) At end of life
(c) Lamp without Iodine at end of life

In the lower-temperature region outside this zone, both iodine recombination and tungsten-iodine formation occur, giving rise to an equilibrium condition for both reactions (i) and (ii). This governs the relative concentrations of monatomic and molecular iodine at any point in the temperature field together with the thermal-diffusion rates of the various constituents. The quantitative determination of the exact processes occurring is complex. In practical terms, the recombination and diffusion rates are functions of the nature and pressure of the inert-gas filling as well as the temperature.

Iodine atoms which reach the lamp wall either recombine or associate with tungsten atoms, the heats of reaction being lost at the wall, which acts as the "third body." The relative magnitudes of tungsten-iodine formation at the wall or in the lamp volume probably depend upon the iodine-atom concentration at the wall. This increases with wall temperature but decreases with increasing gas pressure, which favors greater iodine formation in the lamp volume. If the wall temperature is greater than 250°C, the tungsten iodide formed remains as

a vapor and diffuses away, remaining stable up to a temperature of about 1200°C, after which there is an increasing tendency for decomposition as the temperature rises nearer the filament. (The iodine is then regenerated and the tungsten-vapor density near the filament is increased.)

If, however, the wall temperature is below about 250°C, the tungsten iodide formed condenses as a brown film. The iodine is thus withdrawn permanently from the vapor phase, leading to such depletion that the wall quickly blackens with evaporated tungsten and the iodine cycle is destroyed. It is, therefore, important that all parts of an iodine lamp are above a temperature of 250°C.

The maximum wall temperature for prevention of wall blackening is governed by the temperature stability of the tungsten-iodide molecule and is higher than the devitrification temperature of fused silica and the softening point of the hardest glass.

See FIGURE 1.2.1

FIGURE 2.2.1 shows the typical reactions as a function of temperature between tungsten and iodine.

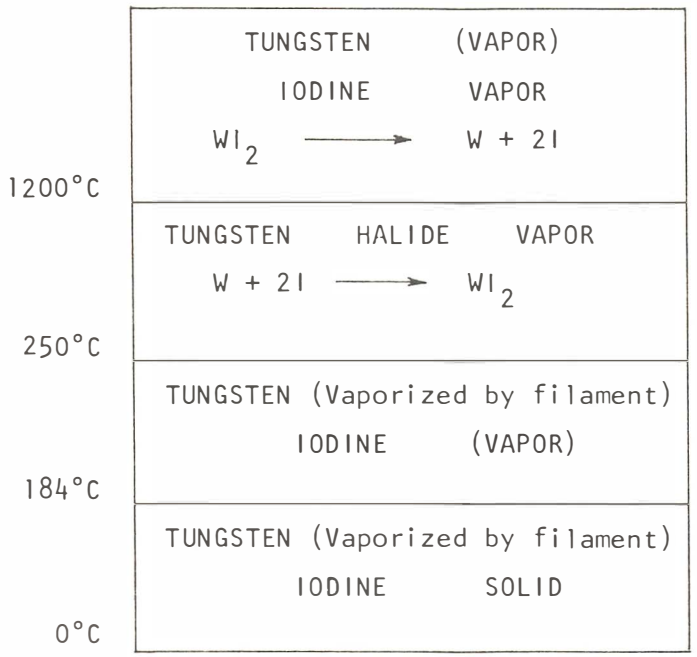


FIGURE 2.2.1

2.3 Iodine Lamp Performance

The well known characteristic exponents relating life, efficiency, filament temperature and voltage are virtually unchanged. However, iodine lamps may be operated at over 30% higher efficiency than conventional lamps.

This improvement is largely a result of the higher operating pressure developed in the iodine lamp because of its high wall temperature and small volume, rather than by the iodine-tungsten cycle.

The pressure of iodine vapor necessary for successful regenerative action is low at a few millimetres of mercury. At such a pressure, its optical absorption has negligible effect on the light output of an operating lamp, although the pink color of the iodine vapor can be seen at the iodine-introduction stage during processing.

The light loss due optical absorption can be as high as 7% in heavily dosed iodine lamps.

Owing to the clean wall conditions throughout life, and the prevention of overall tungsten loss from the filament, the light-intensity and current maintenance throughout life is almost 100%.

2.4 Operating Conditions or Positions

Under all conditions, no part of the bulb wall must be less than 250°C. In most cases, the hottest part of bulb wall operates in excess of 600°C.

Vertical operation of long tubular iodine lamps is liable to produce blackening at the upper end, due to diffusion separation of the inert gas and iodine vapor, the latter accumulating in the lower end of the lamp. The phenomenon is a function of iodine pressure, the nature and pressure of the inert-gas filling and the lamp bore and length.

2.5 Lamp Life and Lumen Maintenance

Iodine lamp life is largely a matter of whether the filament fails due to tungsten evaporation or due to contaminates which accelerate tungsten loss.

Owing to the necessarily high envelope temperature and the vigorous chemical reactivity of iodine, the iodine lamp is extremely sensitive to gaseous or solid impurities likely to emanate from the envelope material, the filling gas, the filament or the iodine itself. The notorious water-vapor cycle which accelerates tungsten redistribution along the filament coil can seriously shorten iodine-lamp life and induce lamp blackening if the iodine concentration is insufficiently high. Traces of oxygen or tungstic oxide lead to severe end erosion at the filament tail resulting in premature failure. Certain metallic impurities such as iron seriously interfere with the tungsten-iodine reaction cycle and cause lamp blackening. Lamp blackening or loss of lumen maintenance occurs when the rate of tungsten transferred to the bulb wall is greater than the return of tungsten from the wall to the filament by the halogen cycle.

2.6 Effect of Impurities on Blackening

IRON

NICKEL

COPPER

These materials produce heavy iodide deposits in the corners of the lamp with no blackening that can be directly attributed to the contaminates. If blackening occurs, it is because the iodine level has been reduced due to combining with the contaminates.

2.6.1 Quartz Powder

No effect on blackening even in considerable quantities.

2.6.2 Brass

This material results in a greyish deposit in exhaust tubulation area.

2.6.3 Fe_2O_3

This material results in large reddish deposits of FeI_2 in corners (low bulb temperature areas) after several hours of burning and also increased H_2O cycle activity.

2.6.4 Aluminum

Aluminum is one material which results in heavy blackening on overnight age (10 hours). Lamps which contain Al_2O_3 do not

result in blackening. This may be a good indication that Al is an oxygen getter in iodine lamps. (See effect of Oxygen).

2.6.5 Graphite

Small amounts of graphite do not cause blackening, or loss of lamp life.

2.6.6 Mercury

Mercury has essentially the same effect as Al.

2.6.7 Carbon

Carbon seems to be required for efficient operation of the regenerative cycle. The reactions involved in the regenerative cycle are complex and not fully understood.

The following were suggested by analysis of the normal fill gas after burning, and by the effect of variations in the normal fill-gas composition on blackening and life:

$$2C + O_2 \rightleftharpoons 2CO$$

$$2CO \rightleftharpoons CO_2 + C$$

$$CO_2 \rightleftharpoons CO + O$$

The water cycle cannot operate in the presence of a large amount of carbon, since carbon will preferentially tie up oxygen and/or hydrogen. This may be an additional important function of the carbon addition, but the primary function of the carbon is considered to be oxygen transport via carbon.

2.6.8 Oxygen

The addition of O_2 to the I_2-Argon mixture results in a substantial decrease in the number of lamps which blacken when no O_2 is present. The addition of Oxygen in pressure less than 1 torr has little or no effect on life.

If the initial O_2 pressure is greater than 1 torr, a blue tungsten oxide deposit appears on the ends of the lamp after several minutes of operation and early life failures usually occur.

A typical fill for a T-3 lamp would be:

1.1μ moles I_2
600 torr Argon
50-150 microns Oxygen

On this basis, the initial O_2 pressure is approximately 0.01 - 0.03% of the total pressure.

The fundamental role of O_2 in prevening blackening in I_2 lamps is not obvious. The initial O_2 pressure (50-150μ) is only 0.01-0.03% of the total pressure and this is approaching the purity limit of the Ar. A mass spectrometric analysis lamp containing larger quantities of O_2 (2-5 mm) and operated for several hours show no O_2 present in the gas phase. This would indicate that the O_2 remained on the bulb wall as $W(O)_x$ and that possibly this oxide surface then acted as a good catalytic surface for the formation of WI_2.

Lamps which have been baked out, flashed in O_2 to form a layer of $W(O)_x$ on the bulb wall, blackened by high temperature filament operation, and filled with the usual I_2-Ar mixture, clean up after a short period of time at rated voltage. Clean up is complete in 5-10 seconds. All of the lamps show complete and rapid clean up of W which was deposited on the $W(O)_x$ layer. A reverse of the process has the same results. That is, a deposit of W with $W(O)_x$ on top acts the same as a deposit of $W(O)_x$ with a layer of W on top. The inconsistency of cleanup in lamps which contain I_2 and Argon compared to those containing a small amount of oxygen proves that some oxygen is desireable and necessary in a tungsten iodide lamp.

2.6.8.1 Effect of Excess Oxygen

When O_2 in excess of 1 mm was added to a T-3 lamp containing the usual I_2-Ar mixture, there is activity at the supports that was quite different from that described above and attributed to the H_2O cycle. After a short period of normal operation, the two support turns around the filament and the first filament turn on each side of the supports are etched and had a very smooth surface. W deposits are observed on the second, third and fourth filament turns and excessive crystal growth occurred on the side

of the filament turn toward the support. In this type of activity, the support turns and first filament turn are attacked and W was transferred to the adjacent filament turns which were operating at a higher temperature. In the H_2O cycle activity, W was transferred in the opposite direction; the fourth or fifth filament turn was attacked and W was transferred to the support and adjacent filament turns which were operating at a lower temperature. Optical pyrometer measurements on lamps show that the temperature increased on successive filament turns from the support and reached a maximum at approximately the fifth turn. The O_2 appeared to attack the cooler areas, i.e., the support turns while the H_2O attacked the fourth or fifth turn from the support where the temperature was near the maximum.

2.6.9 Hydrogen

When a quantity of H_2 greater than stoichrometric (correct proportion for chemical balance) is added to an I_2-Ar filled lamp, life decreases due to H_2O cycle.

When the I_2 was in stoichrometric excess there is often an increase in life.

When H_2 at a pressure equal to or greater than 4.5 mm is added to a lamp containing 1 μ mole of I_2, the lamp becomes almost colorless after several seconds of normal operation indicating the almost complete conversion of the I_2 to HI.

EXPERIMENTAL DATA

A pair of T-3 lamps, both containing 0.92 μ moles of I_2 and 100 mm of Ar and one containing 4 mm of H_2, were operated simultaneously under identical conditions. The lamps were operated horizontally to avoid the complications of the thermal diffusion separation effect and were examined periodically under a low power microscope. The microscopic examination of the lamp containing only I_2 and Ar showed no change in the filament or support turns around the filament during 83 hours of normal operation. The lamp containing the 4 mm of H_2, however, showed a light deposit of W (rough surface appearance) on the support turns around the filament after 24 hours of operation and a light deposit of W on the 3 filament turns on each side of the support after 50 hours of operation. At the conclusion of the experiment (83 hours), a heavy deposit of W was observed on the first 4 filament turns on each side of the support while the 5th turn in each position was considerably smaller in diameter than a normal turn. When the lamp was turned off, the filament ruptured at one of these 5th turn positions due to contraction during cooling.

A second pair of lamps containing the same quantities of I_2 and H_2 but 50 mm of Ar was operated for a total of 52 hours. The same general pattern was followed and the test was completed when the lamp containing the H_2 failed at the 5th turn from one of the supports. The other 5th turns were all smaller in diameter than a normal turn and heavy W deposits were observed on the support turns around the filament and the adjacent 4 turns on each side of the support. The lamp containing no H_2 showed no change in the filament or supports during 52 hours of operation.

Three lamps, all containing 0.92 μ m I_2 and 600 mm of Ar with 2 of the lamps containing 4 mm of H_2, were operated simultaneously for a total of 120 hours. Temperature measurements were made periodically on the support turns and adjacent filament turns with an optical pyrometer. The lamp containing no H_2 showed no change during operation while the 2 lamps containing H_2 showed a decrease in temperature of the support turns around the filament and adjacent filament turns due to the preferential deposition of W on these areas.

The effect of the 4 mm of H_2 in these lamps was to initiate an H_2O cycle by the reduction of the quartz walls by Hydrogen atoms. The H_2O cycle increased the rate at which W reached the wall and consequently the rate at which the W was returned to the vicinity of the filament by the I_2 cycle was increased. This increased activity and the effect of preferential deposition of W on cooler areas resulted in the heavy deposits of W on the vicinity of the supports in a relatively short time. The rate at which the W was desposited on the cooler areas increased with decreasing Ar pressure as would be expected. All lamps were substantially clean at the end of life and in almost all cases, the end of life resulted from rupture of the filament in the immediate vicinity of one of the supports.

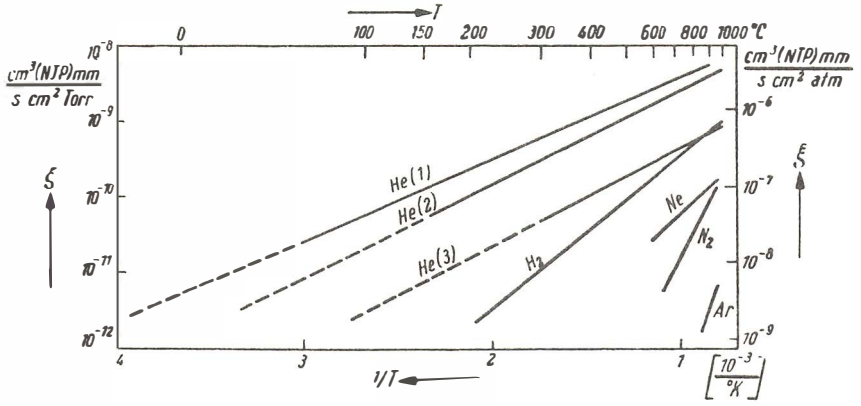
Lamps containing less than 4 mm H_2, (an excess of I_2).

Life is longest when I_2 is in excess of H_2.

The efficiency of formation of HI is demonstrated by the almost complete disappearance of the characteristic pink color of I_2 in a lamp containing a stiochiometric quantity of H_2 and operated for a short time. The lamps contained an excess of I_2 which would have insured the almost complete conversion of H_2 to HI either in a homogeneous gas phase reaction or a hetergeneous reaction on the wall. In any event, H atoms were not available to reduce the quartz and evidently the HI did not react with the quartz to produce H_2O at an appreciable rate. The explanation satisfactorily accounts for the absence of a prominent H_2O cycle in lamps containing an excess of I_2 and thus accounts for the fact that the life of these lamps is at least as long as the lamps containing no added H_2.

HYDROGEN CONTROL DURING LIFE

Hydrogen which is not combined with iodine will escape from the bulb through the quartz walls. The rate varies with wall thickness and wall temperature.



Permeability ξ of fushed silica to various gases as function of temperature T(°C) and of $1/T$(°K)

ORDER OF FLOW OF ATMOSPHERIC GASES INTO SiO_2 BULB AT 25°C (FOR 1 MM THICK, 1 cm^2 AREA)

Gas	Atmospheric abundance C (cm, partial pressure)	Permeation P (cm^3 STP/sec for 1 cm Hg gas pressure difference)	Inflow $\xi \times P$ (cm^3/sec)	Order of Inflow	Atoms/sec
N_2	59.5	2×10^{-29}	1.2×10^{-27}	5	
O_2	15.9	1×10^{-28}	1.6×10^{-27}	4	
A	0.705	2×10^{-29}	1.4×10^{-29}	6	
Ne	1.8×10^{-2}	2×10^{-15}	3.6×10^{-17}	2	900
He	4.0×10^{-4}	5×10^{-11}	2.0×10^{-14}	1	500,000
H_2	3.8×10^{-5}	2.8×10^{-14}	1.0×10^{-18}	3	25

Consequently, in long life lamps containing initial Hydrogen, sufficient hydrogen may be lost by permeation to nullify any beneficial effect.

CARBON MONOXIDE

In incandescent lamps without iodine, and with added CO, early failure has been shown to occur due to a CO - CO_2 - W cycle.

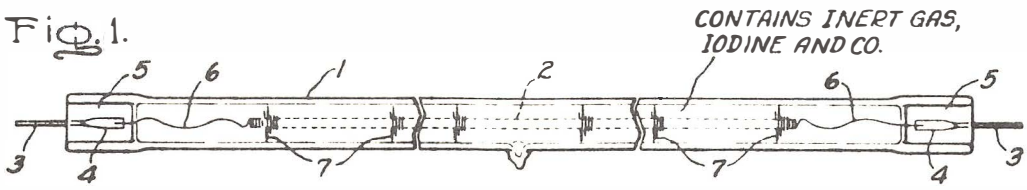
This is believed to come about through a series of reactions as follows: in regions of lower temperatures away from the filament there would be the reaction $CO + CO \rightarrow CO + C$; at the filament, the reaction $W + CO_2 \rightarrow WO_x + CO$; and at the envelope wall the reaction $WO_2 + 2CO \rightarrow W + CO_2 + CO$. The cycle could be stopped by freezing out CO_2.

It would therefore be expected that in lamps containing iodine the CO cycle would similarly cause filament attack like that attributed to the water cycle, since CO_2 released oxygen at the hot filament as does H_2O. In fact, tests of iodine-containing lamps carefully made to avoid contaminants and filled with 15 to 50 mm Hg of CO in addition to the inert fill gas and iodine, showed that they failed in less than 50 hours. Although the lamp envelope remained clean, the filament failed by transfer of tungsten down the thermal gradient from a hotter filament coil turn to a cooler turn, resulting in thinning and burning out a filament turn close to one of the filament supports. Thus, although the tungsten-iodine cycle was operating due to the oxygen released at the hot filament, the lamps were failing early in life by virture of a CO-CO_2-W cycle.

However, completely different results were obtained with various small amounts of CO added to the fill gas, particularly in amounts of about 0.2 to not more than 7.5 mm. Hg of CO correlated in proper relation to fill gas pressures of about 1200 to about 5000 mm Hg.

The beneficial affects of added small amounts of CO were confirmed in a number of tests, particularly in tests with 1500 watt and 500 watt lamps of the type shown in FIGURE 1 and described above.

Fig. 1.



For the 1500 watt lamps operating at a true filament temperature of about 3000°K, FIGURE 2 shows the amount of CO necessary to maintain the lamps clear and free from blackening at different pressures of the argon fill gas. The CO content along the curve range between about 4.7 to about 0.5 mm Hg for argon pressures ranging from about 1200 to about 5000 mm Hg. Amounts of CO above the curve produce clean lamps whereas amounts of CO below the curve result in darkening by tungsten deposits on the envelope.

Fig. 2.

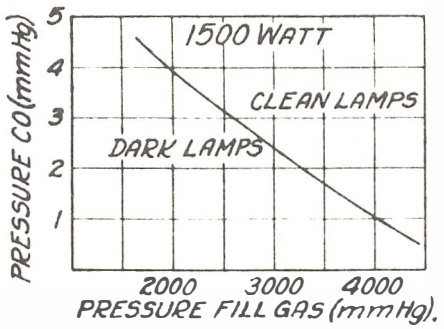
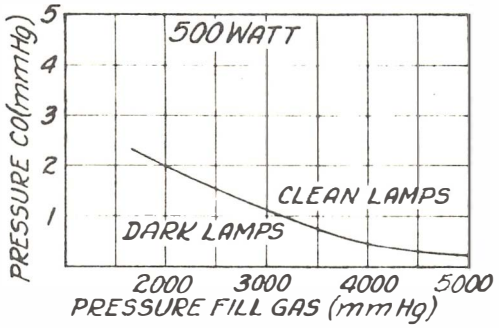


FIGURE 3 shows the results obtained with the 500 watt amps also operating at a filament temperature of about 3000°K. In this case the CO content along the curve varies between about 2.3 and 0.2 mm Hg for argon fill pressures ranging from about 1400 to 5000 mm Hg.

Fig. 3.



It was clearly evident from the appearnace of the lamps that the carbon monoxide was controlling lamp darkening, and that the required amount of carbon monoxide decreased with increased fill gas pressure. Taking into account the finding that oxygen accelerates the regenerative iodine cycle

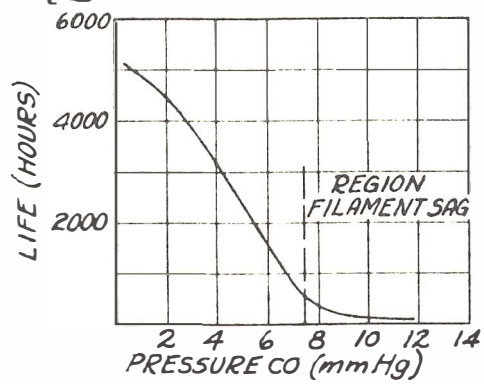
and the effect of CO in generating oxygen, a CO-CO_2-W cycle would explain the observed lamp performance.

It is believed that the explanation for the different amounts of CO required for the 1500-watt lamp of FIGURE 2 and the 500-watt lamp of FIGURE 3 is simply the slower generation of CO_2 in the longer 1500-watt lamp because the cooler "end chambers" (i.e., the end portions containing the straightened legs), which favor CO_2 generation, are a smaller fraction of total lamp volume. Thus, whereas 500-watt lamps remained clean on burning at both normal and over voltage with 2 mm of CO, the 1500-watt lamps darkened with 2 mm of CO and required about 3 mm of CO to stay clean on normal burning and 4 mm of CO on over-voltage burning.

Whereas FIGURES 2 and 3 illustrate the effect of CO content in maintaining the lamps free from blackening, they do not take into account lamp life which, as pointed out above, is severely shortened by the presence of excessive amounts of CO. (Failure then is due to a heavy cycling attack with the transfer of tungsten down the thermal gradient.)

The relationship of lamp life and CO content is illustrated by the curve in FIGURE 4 of tests of 500-watt lamps containing about 2200 mm Hg of argon and operating at a filament temperature of about 3000°K. It will be seen that life decreases rapidly with increasing amount of CO, and amounts of CO exceeding about 7.5 mm Hg result in a significant sagging of the filament.

Fig. 4.



The reactions of carbon monoxide in the regenerative cycle are complex and not fully understood. However, small amounts of carbon monoxide seem to be required for efficient operation of the regenerative cycle.

The most likely explanation is that CO is the active agent which supplies the small but uniform amount of oxygen in the form of CO_2 required to keep the cycle going.

2.7 Bulb Wall Temperature

The I_2 cycle can be operated successfully, i.e., with no blackening during operation, with the wall temperature in the range 250-1000°C. Ordinarily, the reaction between W and I_2 requires a temperature of 800-900°C. The fact that the cycle does operate with the wall temperature as low as 250°C indicates that the reaction occurs between W and I atoms which are produced by the pryolysis of I_2 molecules in the vicinity of the filament. The reaction probably occurs on the wall between adsorbed W and I atoms and the wall temperature is relatively unimportant over a wide range compared with the availability of I at the wall. The wall temperature should be high enough to desorb the WI_2 and consequently a lower temperature limit should exist. An upper limit should also exist since the I atom concentration adsorbed on the bulb wall would be a function of the wall temperature. However, this limit may be beyond the normal operating temperature limit of the quartz.

2.8 Filament Temperature

The actual temperature required for the decomposition of the $WI_2(g)$ molecule is known thermodynamically, the stability of WI_2 reaches a maximum of 1400°K. The lowest filament temperature at which WI_2 was decomposed in a T-3 lamp was 1700°K which was considerably below the normal operating temperature of an incandescent filament. At 1700°K, it was not determined whether the decomposition occurred on the surface of the filament or in the gas phase. In normal operation of a T-3 lamp, it is believed that the $WI_2(g)$ is decomposed in the gas phase in the vicinity of the filament. In other words, the I_2 does

not redeposit the W on the filament but rather returns it to a point near the filament. Once the $WI_2(g)$ is decomposed, the W can then diffuse to the filament and redeposit or it can diffuse to the wall. The closer the point of decomposition of WI_2 to the filament, the greater the probability that the W will be redposited on the filament rather than returning to the wall.

2.9 Iodine Concentration

The I_2 concentration should be as low as possible due to the intense absorption of visible radiation by the I_2 molecule. Aside from this consideration, there appeared to be no upper limit for the successful operation of the cycle. The lower limit is extremely difficult to determine due to the presence of varying quantitites of impurities, e.g., Fe and Mo which formed stable iodides in the cooler areas (corners) of the lamp. Also, the quantity of I_2 required to prevent blackening depends on the rate at which W is reaching the wall which is a function of the filament temperature, the filament to wall distance and the H_2O cycle activity.

2.10 COMMERCIAL TUNGSTEN HALOGEN LAMP DATA

Tungsten Halogen Lamps Listed by Amps (Including Airport)

Watts	Bulb	Base	NAED	Ordering Abbreviation	Amps	Std. Case Qty.	Description	Lighted Length Inches	Class and Fil.	Avg. Rated Hours Life	Approx. Lumens	M.O.L. Inches
45	T-2½	1¾" Perp. Lead	58804	6.6A/T2½Q/ICL-45	6.6	12	Perpendicular Lead Base Clear (23, 71, 73, 93)‡	.173 Max.	C, C-8	2000	675	2
115	T-5	2 Pin Pf	58798	6.6A/T5Q/CL/2PPF-115	6.6	12	Clear Airport (23, 71, 93)‡	L.C.L. 1.54	C, C-BAR6	500	2400	2.56
200	PAR-64	Mog. End Prong	56220	6.6A/PAR64Q/2P	6.6	12	Vasi-Airport Burn Base down to horizontal‡ (106)		C, CC-6	2000		4½
	T-4	1¾" Perp. Lead	58801	6.6A/T4Q/1CL-200	6.6	12	Perpendicular Lead Base Clear (23, 71, 73, 93)‡	.256 Max.	C, CC-8	700	5500	3 1/16
		D.C. Bay Ring	58746	6.6AQ/CL/DCR	6.6	12	Clear, Airport (23, 71, 93)‡	L.C.L. 1 1/16	C, CC-6	500	5200	2⅜
300	PAR64	Mog. End Prong	56221	Q6.6A/PAR64/3P	6.6	6	Vasi-Airport Burn Base down to horizontal‡ (106)		C, CC-6	2000		4½

TUNGSTEN HALOGEN

Watts	Bulb	Base	NAED	Ordering Abbreviation	Volts	Std. Case Qty.	Description	Lighted Length Inches	Class and Fil.	Avg. Rated Hours Life	Approx. Lumens	M.O.L. Inches
300	T-2½	RSC	58923	300T2½Q/CL	120	12	Clear (71, 87, 93)‡ (ANSI Code — EHM)	2⅛	C, C-8	2000	6000	4 11/16
	T-4	RSC	58942	300T4Q/CL	120	12	Clear (23, 71, 93, 95)‡ (ANSI Code — EHP-120V)	⅝	C, CC-8	2500	5000	3⅛
			58943	300T4Q/CL	130	12	Clear (23, 71, 93, 95)‡	⅝	C, CC-8	2500	5000	3⅛
400	T-4	RSC	58936	400T4Q/CL	120	12	Clear (23, 71, 93. 95)‡ (ANSI Code — EHR-120V)	⅝	C, CC-8	2000	7500	3⅛
500	T-3	RSC	58883	500T3Q	120	12	Frosted (71, 87, 93)‡ (ANSI Code — FCZ)	2	C, C-8	2600	3500	4 11/16
			58856	500T3Q/CL	120	12	Clear (71, 87, 93) (ANSI Code — FCL)	2	C, C-8	2600	10000	4 11/16
			58902	500T3Q/CL	130	12	Clear (71, 87, 93)‡	2	C, C-8	2600	10000	4 11/16
	PAR-56	Mog. End Prong	56210	500PAR56Q/NSP	120	12	Narrow Spot (29, 44)		C, CC-6	4000	7000	5
			56211	500PAR56Q/MFL	120	12	Med. Flood (29, 44)		C, CC-6	4000	7000	5
			56212	500PAR56Q/WFL	120	12	Wide Flood (29, 44)		C, CC-6	4000	7000	5
1000	PAR-64	Ext. Mog. End Prong	56206	1000PAR64Q/NSP	120	6	Narrow Spot (29, 44)		C, CC-6	4000	16000	6
			56207	1000PAR64Q/MFL	120	6	Med. Flood (29,44)		C, CC-6	4000	16000	6
			56208	1000PAR64Q/WFL	120	6	Wide Flood (29, 44)		C, CC-6	4000	16000	6
	T-3	RSC	58948	1000T3Q/CL	240	12	Clear (71, 87, 93)‡	6¾	C, C-8	2000	21500	10 1/16
	T-6	RSC	58937	1000T6Q/CL	120	12	Clear (23, 71, 93, 95)‡ (ANSI Code — DWT-120V)	1⅛	C, CC-8	2000	22000	5⅝
1500	T-3	RSC	58859	1500T3Q/CL	208	12	Clear (71, 87, 93)‡	6¾	C, C-8	3000	29000	10 1/16
			58857	1500T3Q/CL	240	12	Clear (71, 87, 93)‡	6¾	C, C-8	3000	29000	10 1/16
			58858	1500T3Q/CL	277	12	Clear (71, 87, 93)‡	6¾	C, C-8	2000	33600	10 1/16

‡Use in equipment with a suitable screen to protect people and surroundings.

SUPER Q TUNGSTEN HALOGEN LAMPS

Super Q Tungsten Halogen Lamps

Watts	Bulb	Single Base	NAED	Ordering Abbreviation	Volts	Std. Case Qty.	Description	L.C.L.	Class and Fil.	Avg. Rated Hours Life	Approx. Lumens	M.O.L. Inches
75	T-3	Miniature Screw	58876	75Q/CL	28	12	Clear (23, 71, 93)[a]	1 3/16	C, CC-6	2000	1400	2 1/4
100	T-4	Mini-Can	58761	100Q/CL	120	12	Clear (23, 71, 93, 95)[a] (ANSI Code — ESN-120V)	1 3/8	C, CC-2V	1000	1900	2 3/4
100	T-4	D.C. Bay	58755	100Q/CL/DC	120	12	Clear (23, 71, 93, 95)[a] (ANSI Code — ESR-120V)	1 3/8	C, CC-2V	1000	1900	2 7/16
			58757	100Q/DC	120	12	Frosted (23, 71, 93, 95)6 (ANSI Code — ETD-120V)	1 3/8	C, CC-2V	1000	1900	2 7/16
150	T-4	Mini-Can	58735	150Q/CL	120	12	Clear (23, 71, 93, 95)[a] (ANSI Code — ETG-120V)	1 1/2	C, CC-8	2000	2600	3
		D.C. Bay	58741	150Q/CL/DC	120	12	Clear (23, 71, 93, 95)[a] (ANSI Code — ETC-120V)	1 1/2	C, CC-8	2000	2600	2 3/4
		Mini-Can	58736	150Q	120	12	Frosted (23, 71, 93, 95)[c] (ANSI Code— ETH-120V)	1 1/2	C, CC-8	2000	2500	3
		D.C. Bay	58737	150Q/DC	120	12	Frosted (23, 71, 93, 95)[a] (ANSI Code— ETF-120V)	1 1/2	C, CC-8	2000	2500	2 3/4
			58739	150Q/CL/DC/1	120	12	Clear (23, 71, 93, 95)[a] (ANSI Code—ESP-120V)	1 3/8	C, CC-2V	1000	2600	2 7/16
250	T-4	Mini-Can Screw	58762	250Q/CL	120	12	Clear (23, 71, 93, 95) [a] (ANSI Code — EHT-120V)	1 5/8	C, CC-8	2000	5000	3 1/8
			58764	250Q/CL	130	12	Clear (23, 71, 93, 95) [a]	1 5/8	C, CC-8	2000	5000	3 1/8
		D.C. Bay	58720	250Q/CL/DC	120	12	Clear (23, 71, 93, 95)[a] (ANSI Code — ESS-120V)	1 5/8	C, CC-8	2000	5000	3 1/8
		Mini-Can Screw	58763	250Q	120	12	Frosted (23, 71, 93, 95)[a] (ANSI Code — ESM-120V)	1 5/8	C, CC-8	2000	4800	3 1/8
			58765	250Q	130	12	Frosted (23, 71, 93, 95)[a] (ANSI Code—ESM-130V)	1 5/8	C, CC-8	2000	4800	3 1/8
		D.C. Bay	58753	250Q/DC	120	12	Frosted (23, 71, 93, 95)[a] (ANSI Code—ETB-120V)	1 5/8	C, CC-8	2000	4800	3 1/8
			58754	250Q/DC	130	12	Frosted (23, 71, 93, 95)[a]	1 5/8	C, CC-8	2000	4800	3 1/8
500	T-4	Mini-Can Screw	58767	500Q	120	12	Frosted (23, 71, 93, 95)[a]	2	C, CC-8	2000	9500	3 3/4
			58768	500Q	130	12	Frosted (23, 71, 93, 95)[a]	2	C, CC-8	2000	9500	3 3/4
			58766	500Q/CL	120	12	Clear (23. 71, 93, 95)[a]	2	C, CC-8	2000	10000	3 3/4
			58756	500Q/CL	130	12	Clear (23, 71. 93, 95)[a]	2	C, CC-8	2000	10000	3 3/4
750	T-4	Mini-Can	58769	750Q/CL	120	12	Clear 3050°K (23, 71, 73, 93, 95)[a]	2	C, CC-8	500	18500	3 3/4
1000	T-5	Mini-Can	58774	1000Q/3CL	120	12	Clear 3200°K (23, 71, 73, 93, 95)[a]	2.150	C, CC-8	300	29000	3 7/8
1500	T-8	Mog. Scr.	58965	1500Q/CL/48	120	6	Clear (8, 71, 73. 93, 95)[a]	5 1/4	C, CC-8	2000	34000	7

[a]Use in equipment with a suitable screen to protect people and surroundings.

2.11 References for Additional In-Depth Information

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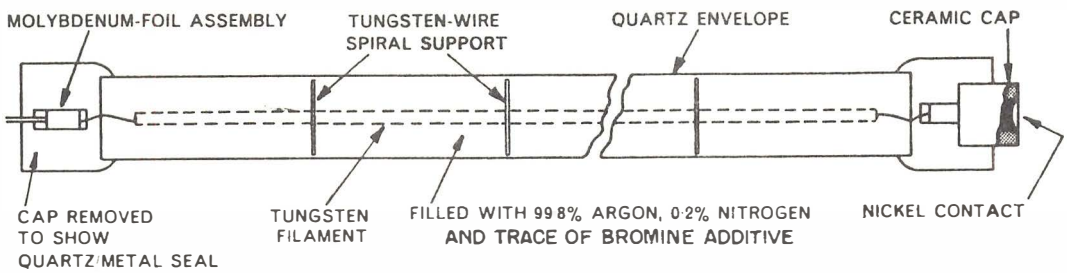
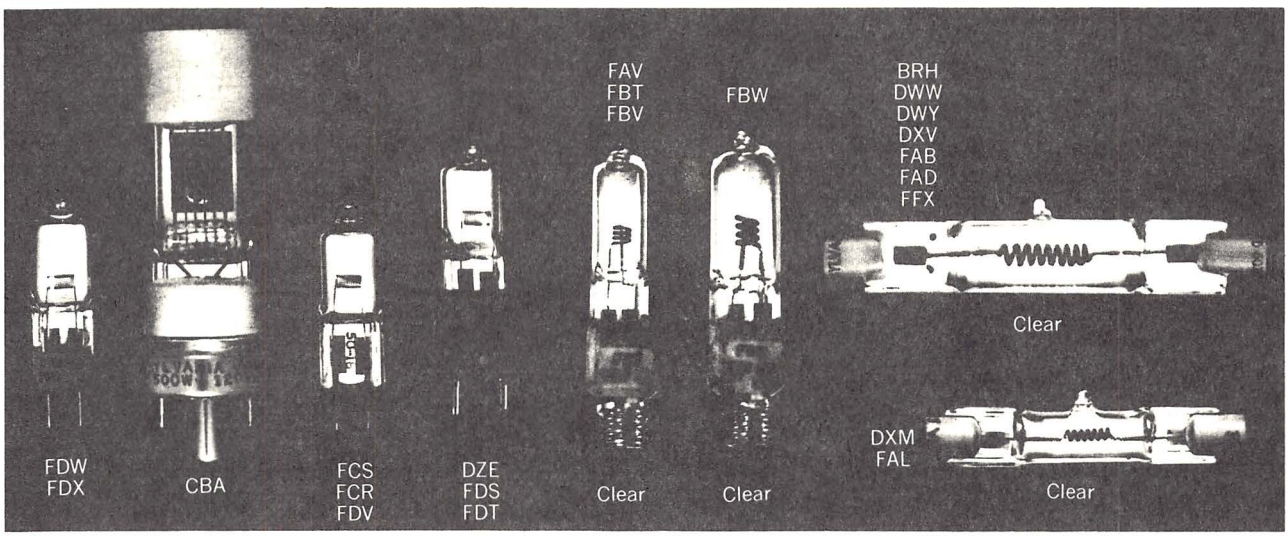
3.0 THE TUNGSTEN BROMINE LAMP

3.1 Construction of typical Tungsten Bromine Lamps





MECHANISM AND CONDITIONS FOR THE BROME REGENERATIVE CYCLE

The bromine-tungsten cycle is dependent on the formation and decomposition of tungsten bomide. The general form of the reactions is as follows:

Tungsten (W) + Molecular Bromine (Br_2) $\longrightarrow$ $W\,Br_x$

Tungsten (W) Atomic Bromine (Br) $\longrightarrow$ $W\,Br_x$

There is a greater tendency for reaction between tungsten and atomic bromine as compared to the molecular forms. In the bromine lamp, the following reaction takes place:

$$W + 3Br_2 \longrightarrow W\,Br_6$$

$W\,Br_5 + Br$

$W\,Br_4 + Br_2$

$W\,Br_3 + Br_2 + Br$

These compounds vaporize above approximately 125°C

$$W\,Br_6 \xrightarrow[\text{To}]{1073 \text{ to } 1325^\circ C} W + 6Br$$

In a tungsten-filament lamp containing inert gas and a partial pressure of bromine, tungsten atoms evaporated from the filament diffuse away towards the bulb walls. Close to the filament the temperatures are too high for combination of tungsten and bromine and the tungsten and bromine behave like independent inert vapors. In the lower temperature region closer to the bulb wall and at the bulb wall, the tungsten and bromine combine and form a gaseous tungsten halide. The quantitative determination of the exact processes occurring is complex and is influenced by other materials which may be in the lamp as deliberate additives or contaminates.

The relative magnitude of the tungsten bromide formation at the wall or in the lamp volume depends on the bromine concentration at the wall. The bromine concentration at the wall increases with wall temperature, but decreases with increaseing gas pressure, which favors greater bromide formation in the lamp volume, If the wall temperature is greater than approximately 120°C, the tungsten bromide formed remains a vapor and diffuses away, remaining stable up to a temperature of about 1300°C, after which there is an increasing tendency for decompositions as the temperature rises nearer the filament. The bromine is then regenerated and the tungsten vapor density near the filament is increased.

If, however, the wall temperature is below about 120°C, the tungsten bromine formed condenses as a blue-black film. The bromine is thus withdrawn permanently from the vapor phase, leading to depletion of bromine and the walls quickly blacken with evaporated tungsten and the bromine cycle is deactivated. It is therefore important that all parts of a bromine lamp are above a temperature of 120°C.

The maximum wall temperature for prevention of wall blackening is governed by the temperature stability of the tungsten-bromide molecule. Experimental data shows the minimum temperature for coating by thermal decomposition of tungsten bromide to be approximately 1100°C and, therefore, this should be the maximum bulb wall temperature.

FIGURE 3.2.1 shows the typical reaction or a function of temperature between tungsten and bromine

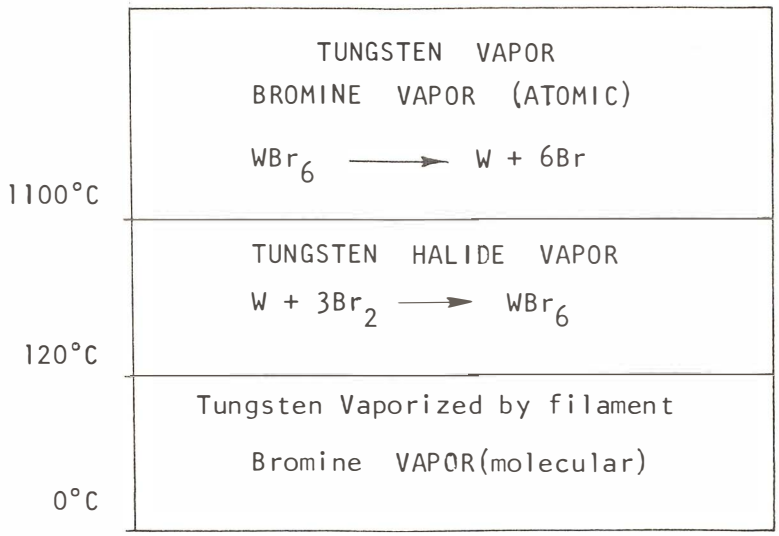


Figure 3.2.1

3.3 BROMINE LAMP PERFORMANCE

The well known characteristic exponents relating life, efficiency, filament temperature and voltage are virtually unchanged. However bromine lamps may be operated at over 30% higher efficiency than conventional lamps.

This improvement is largely a result of the higher operating pressure developed in the bromine lamp because of its high wall temperature and small volume, rather than by the bromine-tungsten cycle.

The pressure of bromine vapor necessary for successful regenerative action is low at a few millimeters of mercury.

Unlike iodine, vaporized bromine is colorless and causes no light loss. In iodine lamps the light loss can be as high as 7%.

Owing to the clean wall conditions throughout life, and the prevention of overall tungsten loss from the filament, the light-intensity and current maintenance throughout life is almost 100%.

3.4 OPERATING CONDITIONS AND POSITIONS

Under all conditions, no parts of the bulb wall must be less than 125°C. In most cases, the hottest part of the bulb wall operates in excess of 400°C.

Single end bromine lamps can be burned in any position. Long linear bromine lamps are usually burned horizontally. Vertical operation is liable to produce blackening at the upper end due to diffusion separation of the inert gas and the bromine vapor. The phenomenon is a function of bromine pressure, the nature and pressure of the inert fill gas and the lamp bore and length. This problem is discussed in detail in Section 23.1 Lamp Design.

3.5 LAMP LIFE AND LUMEN MAINTENANCE

Bromine lamp life is largely a matter of whether the filament fails due to tungsten evaporation or due to contaminates which accelerate tungsten loss.

Owing to the necessarily high envelope temperature and the vigorous chemical reactivity of bromine, the bromine lamp is extremely sensitive to gaseous or solid impurities likely to emanate from the envelope material, the filling gas, the filament or the bromine itself. The notorious water-vapor cycle which accelerates tungsten redistriubtion along the filament coil can seriously shorten bromine-lamp life and induce lamp blackening if the bromine concentration is insufficiently high. Traces of oxygen or tungstic oxide lead to severe end erosion at the filament tail resulting in premature failure. Certain metallic impurities such as iron seriously interfere with the tungsten-bromine reaction cycle and cause lamp blackening. Lamp blackening or loss of lumen maintenance occurs when the rate of tungsten transfer to the bulb wall is greater than the return of tungsten from the wall to the filament by the halogen cycle.

3.6 EFFECT OF IMPURITIES ON BLACKENING

Bromine is far more active than iodine and can still function with impurity levels that would cause failure of the halogen cycle in iodine lamps. However, the amount of bromine in a lamp is more critical than

iodine. Any material which either accelerates the transport of tungsten to the wall or retards the rate at which tungsten is returned to the filament will have significant effect on the life and or lumen maintenance.

3.6.1 Materials which Retard the Bromine Cycle

The substances which slow down the regenerative cycle have a getter effect on the halogen additive within the lamp. Thus, when an alkali, for example sodium, is present, stable sodium halogen compounds are formed which precipitate. With a sufficiently large amount of sodium present, this finally leads to a sufficient deficiency in the amount of halogen available so that the regenerative cycle breaks down with consequent blackening of the lamp. Although it would be possible to postpone the breakdown of the regenerative halogen cycle by using an excess amount of halogen in the lamp, the result of the excess amount of halogen present would be excessive functioning of the regenerative cycle. As a consequence, the more it is attempted to postpone the onset of lamp blackening in this manner, the sooner will the lamp become unserviceable as a consequence of the excess rate of the regenerative cycle.

Sodium	Nickel	Chromium
Potassium	Copper	Boron
Iron	Aluminum	

The compound does not necessarily precipitate, but may vaporize during the lamp operation and still tie up bromine as a stable compound.

3.6.2 Materials which Lower the Activity of Bromine

There is a limit to the concentration of bromine which can be used in a lamp. Because of the activity of pure bromine, bromine will corrode leads and supports at temperatures close to room temperature.

HYDROGEN

When H_2 is present in a lamp with bromine, hydrogen bromide (HBr) is formed during initial lamp operation. If H_2 and Br_2 are added to argon fill gas, the characteristic orange bromine color can be identified. After operation, the lamp becomes colorless indicating a colorless bromine has been formed.

Figure 3.6.2.1 shows the relative life of lamp made using one part H_2 for three parts Br_2 vs lamps made with equal parts H_2 and Br_2.

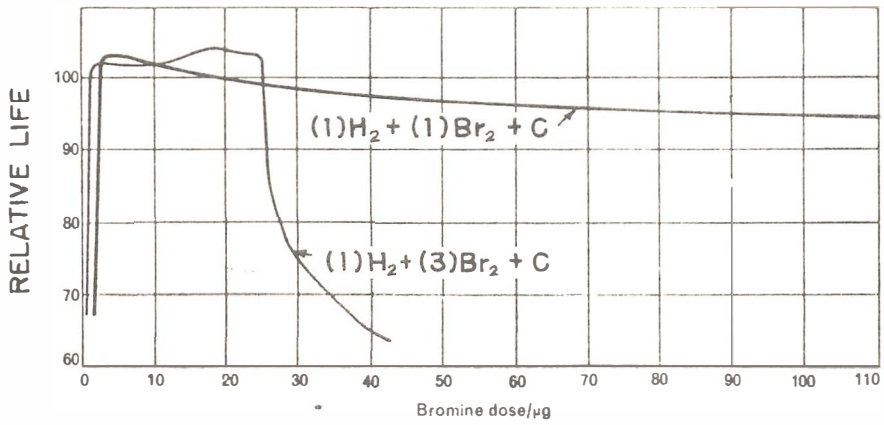


Figure 3.6.2.1

The shapes of the curves for bromoform ($CHBr_3$) and dibromoethane (CH_2Br_2) are similar at the low bromine doses but different for the higher concentrations.

The initial low-quality figures in both cases are due to insufficient bromine to react with the tungsten evaporating from the filament, resulting in bulb blackening and short useful lives. As the doses are increased the lamps remain clean for longer, until no bulb blackening is in evidence when the filament burns out.

On elimination of bulb blackening the quality of the hydrogen ratio dosed lamps is then fairly constant until at approximately 25 µg bromine, when the lamp lives start to be reduced by tail attack. This takes the form of erosion of the filament tail where it enters the pinch seal, coupled with tungsten crystal growths just above this point on the tail. The point of attack of a filament tail is clearly temperature dependent and is usually at the coolest point readily accessible to the bromine. Further increases in bromine dose results in faster erosion of the tail and supports.

The shape of the curve above 2 µg is very different where dibromomethane is the additive. Even at lamp doses of 100 µg bromine no tail attack was observed with dibromomethane. Since over the whole concentration range the

only major difference between the two compounds is their H/Br ratio, the effect of hydrogen in reducing tail attack is clear.

3.6.3 Materials Which Accelerate the Bromine Cycle

The materials which speed up the regenerative cycle cause noticeable transport of tungsten and can be distinguished from surface roughness and dendrite growth on internal lamp components. When the quantity of substances which speed up the regenerative cycle is small, then it is possible to compensate for the negative influence of lamp service life by selection of the amount of bromine additive.

These materials are Carbon Monoxide, Carbon Dioxide, Water Vapor and Oxygen. All of these materials decompose under certain conditions and yield oxygen.

OXYGEN

Studies have shown that the bromine cycle needs some oxygen in the same sense that the iodine cycle needs oxygen. Figure 3.6.3.1 shows the effect of oxygen addition to a particular group of bromine cycle lamps.

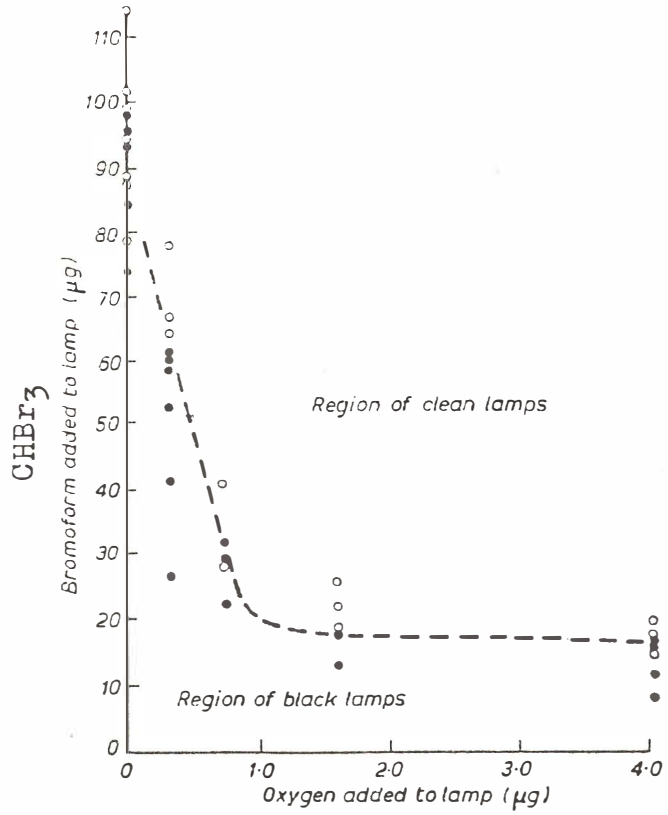


Figure 3.6.3.1 Effect of bromoform and oxygen additions on bulb blackening of 24 V 250 W tungsten-halogen lamps.

The addition of controlled amounts of oxygen to 24 V 250 W tungsten-halogen projector lamps has shown the extreme sensitivity of the bromine cycle to oxygen. Without the addition of oxygen approximately 100 µg of bromoform are required to prevent bulb blackening in this lamp, whereas the addition of 1 µg of oxygen reduces the bromoform required to approximately 20 µg. The rapid increase in bromoform necessary to prevent bulb blackening as the oxygen concentration is reduced below 1 µg suggests that the bromine cycle may not be able to operate in this lamp without the trace amounts of oxygen than can emerge from the lamp components during operation.

The addition of much larger amounts of oxygen, however, can lead to detrimental effects in these lamps by attacking the filament tails resulting in short lamp lives.

The net result is that a little oxygen is good and too much results in short lamp life.

3.6.3.1.1 Methods of Adding Oxygen to a Bromine Cycle Lamp

Oxygen can be added to a lamp in may forms including:

Elemental Oxygen	O_2
Carbon Dioxide	CO_2
Carbon Monoxide	CO
Water Vapor	H_2O

The addition of oxygen can be achieved either through a reduced baking of the bulbs to leave a sufficient amount of water; in other words, oxygen adsorption layer in the glass, or through a direct addition to the fill gas in the form of elemental oxygen or as carbon monoxide.

While it is unimportant thermodynamically in what form the oxygen is added to the reaction system, it certainly is important with respect to the reaction kinetics whether the oxygen is introduced in elemental form or whether it is added in the form of a compound such as carbon monoxide or carbon dioxide. It has been established from experience that the quality of the lamps is dependent on the amount and the form of oxygen addition.

Tests with well made low voltage projection lamps have shown that lamp life and maintenance varies considerably with amount and type of oxygen addition. The following table shows the lamp results.

Bromine Dose - CH_2Br_2 - 10 Torr
Lamp Fill - Argon

Pressure Torr	O_2 Life	CO_2 Life	CO Life
0	65.4	65.4	65.4
0.2	65.2	68.8	86.6
0.4	80.6	79.2	64.8
1.0	50.8	68.0	70.0
2.0	70.0	79.8	80.4
5.0	21.8	64.8	64.4
10.0	18.0	54.8	57.4
15.0	10.0	13.0	44.0
20.0	7.0	10.8	32.6
30.0			14.8
40.0			15.5

The table shows that the lamps have a larger tolerance for CO without affecting lamp life than for CO_2 or O_2. For maximum life the tolerance for elemental oxygen is the least.

The undesirable qualities of excess oxygen can be observed in the operation of the lamp. With the addition of 0.6 Torr O_2 a whiteish film of Tungsten Monoxide can be observed which shows yellow to bluish coloring with greater oxygen addition. With the addition of CO_2 or CO, these films are formed if the additions are in excess of 15 Torr for CO_2 and 40 Torr for CO. Furthermore, the large amount of tungsten crystal growth on the colder areas of the leads can be noticed with the increased oxygen addition.

Figures 3.6.3.2 a, b and c show lamp life as a function of oxygen addition.

A.

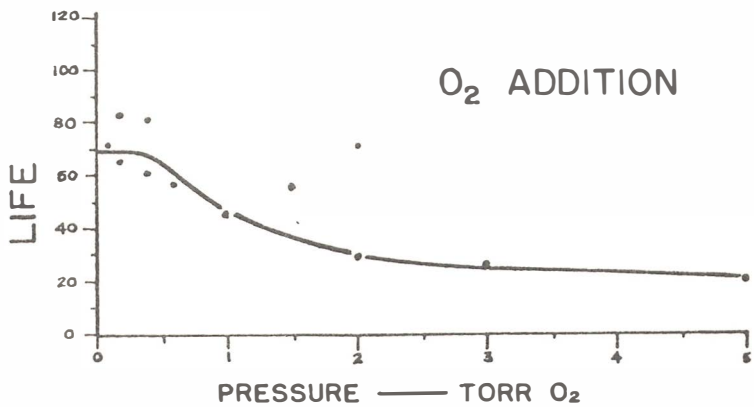
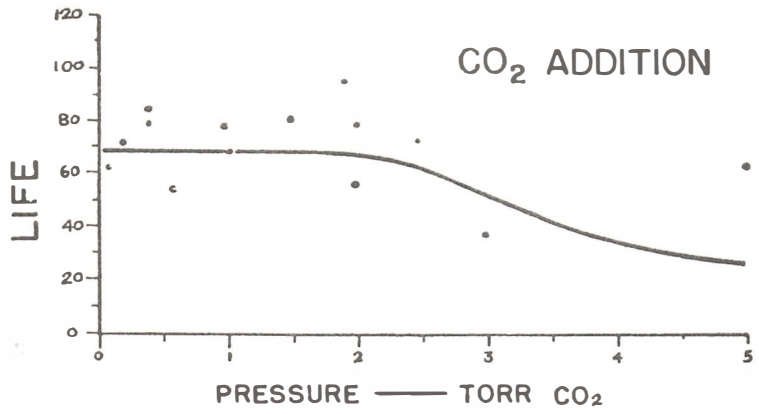


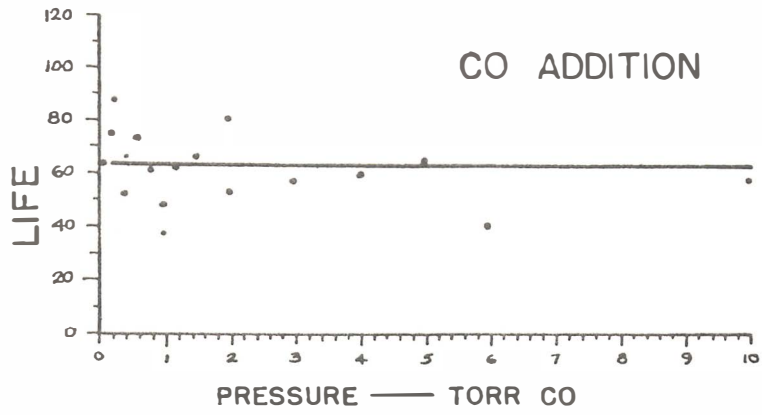
Figure 3.6.3.2

Figure 3.6.3.2 [continued]

B



C



3.6.3.2 Advantage of Carbon Monoxide Additions

At high temperatures, oxygen is in the form of stable carbon monoxide which acts like an inert gas and is practically removed from the reaction process.

At this point, the carbon contained in the bromine additive CH_2Br_2 cannot be ignored. When the temperature of the lamp is gradually raised during light up, at a certain temperature limit, the dibromethane (CH_2Br_2) is irreversibly changed into bromine, hydrogen and carbon. The hydrogen and bromine react with the tungsten which is evaporated from the coil and form tungsten bromide, or with the presence of free oxygen, tungsten oxybromide. The carbon either forms carbon oxide with oxygen which is still present or is precipitated on the bulb wall. Thereby in all probability all the oxygen is not tied up in the form of carbon

monoxide since the necessary number of collisions between oxygen and carbon is not achieved and for the fact that the oxygen at the same time is reacting with the tungsten to form tungsten oxides or to react with the already formed tungsten bromide to form tungsten oxybromide.

A part of the carbon is thereby also deposited on the bulb wall and is eliminated from the reaction process.

This also leaves a corresponding amount of active oxygen in the system. If the oxygen is present in the beginning in the form of carbon dioxide a separation of part of the oxygen from the carbon dioxide has to take place before a reaction with the carbon from the dibromomethane process can take place. However even in this case, part of the carbon on the bulb wall is removed from the reaction system and part of the reactive oxygen is left over.

In contrast with addition of carbonmonoxide, already at the beginning of the reaction process, the oxygen is present in the form of a stable end product. The formation of free reactive oxygen does not take place. Therefore, the advantage of carbon monoxide is that it is stable in high temperature areas like an inert gas and prevents the formation of undesirable tungsten oxides. In the lower temperature ranges the carbon monoxide acts as an oxygen donor. In the lower temperature ranges, the formation of halogen cycle improving compounds is enhanced.

The mechanism is suspected to be as follows:

$CO + WO_x \longrightarrow CO_2 + W + XO$ Low Temp. Condition

$CO_2 + W \longrightarrow WO_x + CO$ Higher Temp. Reaction

CO is the active agent, supplying the small but uniform amount of oxygen in the form of CO_2 required by the halogen cycle.

3.6.3.3 Effect of Added H_2O to Bromine Lamps

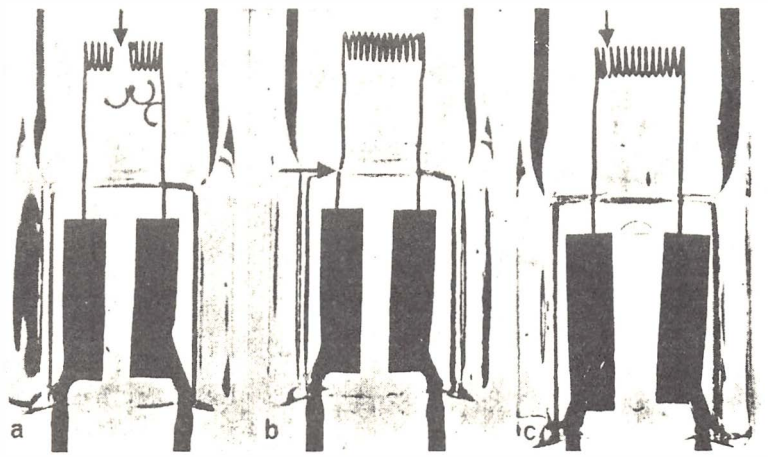
The addition of water to tungsten-bromine lamps would be expected to result in a water - vapor cycle causing erosion of the filament and reduction of lamp life. However, the degree of water cycle for given amount on water added varies depending on the composition and concentration of the bromine additive.

The following table shows the effect of different concentrations of water on $CHBr_3$ and CH_2Br_2 dosed lamps.

EFFECTS OF WATER DOSES

Halogen dose	Water (µg)	Method of failure*	Equivalent ratio H/Br	O/C	O/Br
	0	T	0.33	0	0
33 + 3 µg	0.9	N-T	0.6	0.38	0.13
bromoform	1.5	N	0.75	0.64	0.21
$CHBr_3$	2.2	N-W	0.95	0.93	0.31
	3.0	W	1.2	1.3	0.43
	0	N	0.33	0	0
4.0 $\pm$ 0.6 µg	0.9	W	2.4	3.1	1.0
bromoform	1.5	W	3.7	5.1	1.7
$CHBr_3$	2.2	W	5.3	7.5	2.5
	3.0	W	7.2	10.0	3.4
	0	N	1.0	0	0
32 $\pm$ 1 µg	0.9	N	1.3	0.27	0.14
dibromomethane	1.5	N-W	1.5	0.45	0.23
CH_2Br_2	2.2	W	1.7	0.66	0.33
	3.0	W	1.9	0.90	0.45
	0	N	1.0	0	0
3.5 $\pm$ 0.5 µg	0.9	W	3.5	2.5	1.2
dibromomethane	1.5	W	5.1	4.1	2.1
CH_2Br_2	2.2	W	7.1	6.1	3.0
	3.0	W	9.4	8.3	4.1

*N = Normal, T = Tail, W = water



Types of failure: a, normal; b, tail attack; c, water attack

Three types of filament failure are evident:

(i) Normal failure: failure at a point near the center of the filament coil where it is hottest, probably due to normal evaporation of tungsten. (a)

(ii) Tail failure: the high-dosed bromoform lamps, with little or no added water, failed as expected at the base of the tail where it enters the pinch seal. (b)

(iii) Water failure: the effect of water was observed as thinning of the penultimate turn of the filaments, accompanied by crystal growth on the end turn and upper region of the filament tail. (c)
Lamps affected failed either by melting of the thinning turn or when a crystal growth extended across between the first two turns.

The high-bromine/high-water-content lamps developed reddish-brown deposits in the cool pinch corners during life; these were assumed, although not proven, to be tungsten oxybromides. The high-water/low-bromine lamps showed whitish films on the bulbs early in life, probably a tungsten oxide.

There is evidence of a delicate balance.

With bromine dose that is less than 1:1 ratio of hydrogen, such as bromoform ($CHBr_3$) or pure Br_2, the tolerance to H_2O is higher than HBr or CH_2Br_2 until the 1:1 H/Br ratio is reached.

Above 1:1 H/Br ratio, the lamps fail due to water cycle regardless of composition of bromine additive. With less than 1:1 H/Br ratio, the lamps fail due to lead and tail attack.

3.6.4 Materials Which are Cycled in Same Manner as Tungsten

The bromine halogen cycle operates with many other materials. The following table shows the results of an experiment where tungsten from one filament was deposited on another filament as a coating. The filament and coating were analyzed spectrographically.

MATERIALS IN FILAMENT	PPM	MATERIALS FOUND IN COATING	PPM
Carbon	42 - 86		38
Moly	100 - 500		30 - 100
Sulfur	18		20
Hydrogen	0.86 - 1		0.0007
Oxygen	1 - 140		0.5
Nitrogen	2.9 - 27		0.02
Aluminum	10 - 15		< 1
Boron	< 2		< 0.3
Calcium	< 10		0.4
Chromium	10 - 30		< 1
Copper	1 - 10		0.3
Iron	15 - 90		0.7
Nickel	15 - 60		0.3
Silicon	10 - 90		< 3

The data show that Carbon, Moly, and Sulfur are transported by a halogen cycle in the same manner as tungsten. The remaining materials either do not form compounds with Bromine or form stable compounds with Bromine. It has already been established that Nickel and Iron form compounds which getter halogen and remove it from the halogen cycle permanently.

Additional materials which are known to be subject to the bromine regeneration cycle are as follows:

Silicon	Tantalum	Antimony
Titanium	Chromium	Bismuth
Zirconium	Cobalt	Hafnium
Vanadium	Germanium	Uranium
Columbium	Tin	Rhenium

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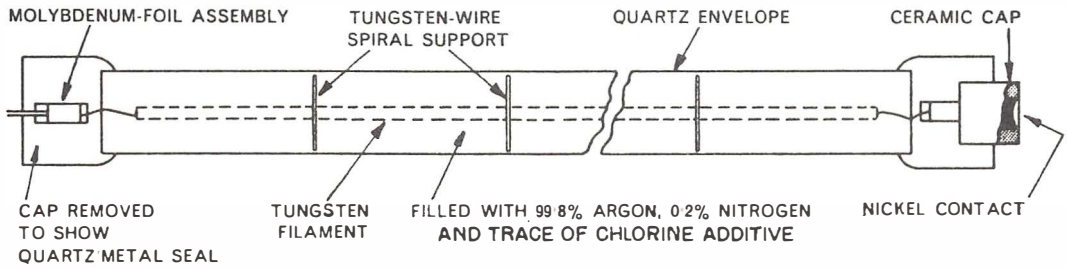
4.0 THE TUNGSTEN CHLORINE LAMP

4.1 Construction of a Typical Tungsten-Chlorine Linear Lamp



The construction of lamps for the chlorine cycle is the same as for bromine lamps.

4.2 Mechanism and Conditions for the Chlorine Regenerative Cycle

The chlorine-tungsten cycle is dependent on the formation and decomposition of tungsten chloride. The general form of the reactions is as follows.

Tungsten (W) + Molecular Chlorine (Cl_2) $\longrightarrow$ WCl_x

Tungsten (W) + Atomic Chlorine (Cl) $\longrightarrow$ WCl_x

There is a greater tendency for reaction between tungsten and atomic chlorine as compared to the molecular form.

In the chlorine lamp, the following reaction takes place:

$$W + 3\,Cl_2 \longrightarrow \begin{matrix} WCl_6 \\ WCl_5 \\ WCl_4 \\ WCl_3 \\ WCl_2 \end{matrix}$$

These materials vaporize above approximately 165°C.

$$WCl_6 \xrightarrow{>1500°C} W + 6Cl$$

Chlorine is more active than bromine and, therefore, it is expected to be more critical in relation to tail attack. The minimum conditions for the chlorine cycle are as follows:

Minimum Bulb Wall Temperature	250°C
Maximum Bulb Wall Temperature	1700°C

The maximum bulb wall temperature for prevention of wall blackening is governed by the temperature stability of the tungsten chloride molecule. Experimental data shows the miminum temperature for coating by thermal decomposition of tungsten chloride (WCl_6) to be approximately 1500°C. Since this value is above the useful temperatures of quartz, the maximum bulb temperature is dictated by the bulb construction material.

Figure 4.2.1 shows the typical reactions as a function of temperatures between tungsten and chlorine.

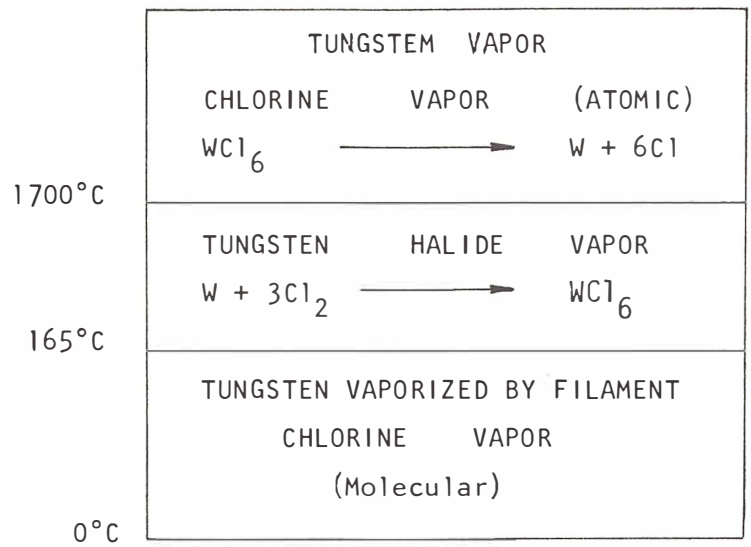


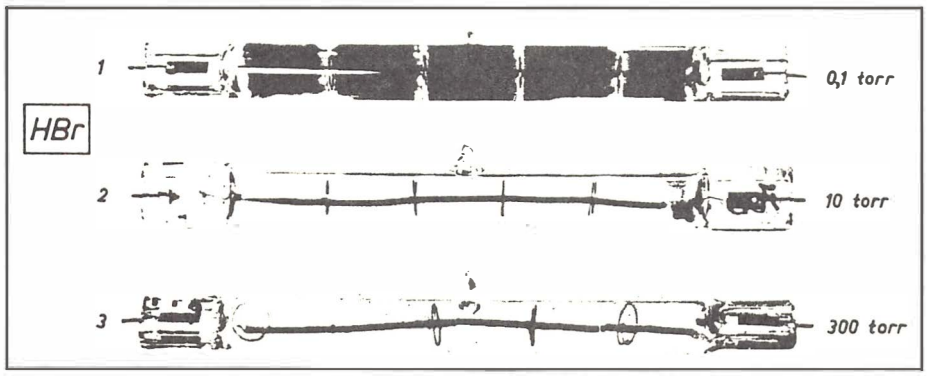
FIGURE 4.2.1

4.3 COMPARISON OF BROMINE LAMPS AND CHLORINE LAMPS

Experimental 225V - 1000 Watt linear lamps made with HBr and HCl added to the argon fill show the following results:

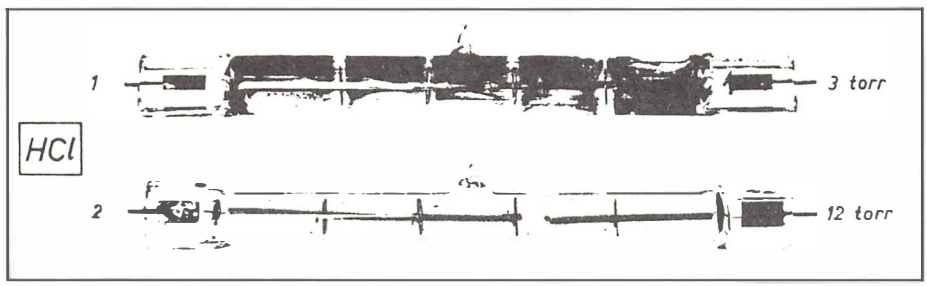
HBr

HBr Dose	Results
0.1 Torr	After 17 hours lamp is intact but blackened
10 Torr	Lamp failed after 28 hours
300 Torr	Lamp failed after 17 hours



HCl

HCl Dose	Results
3 Torr	After 15 hours lamp is intact but blackened
12 Torr	Lamp failure after 33 hours



The data shows the useful partial pressure range of both HBr on HCl to be about the same.

4.3.1 Advantages of Chlorine Over Bromine

A. The chlorine being more active, should be less effected by normal lamp impurities than either bromine or iodine. The chlorine cycle is expected to react with oxygen in the same manner as bromine although there is not only significant experiment work available to verify this.

B. The bulb temperature can be lower in a bromine lamp. Tungsten is attacked by chlorine at close to room temperature. On this basis, chlorine should be superior to bromine in fast cycle lamps where bulb does not get up to steady state temperature conditions.

C. A possible disadvantage is that the dose balance between lamp blackening and tail attack is expected to be more critical than for bromine. On this basis, short life lamps are more suitable for the chlorine cycle than long life lamps.

D. Hydrogen is generally added to chlorine lamps to act as a "buffer" as in bromine lamps. The ratio of H_2 to C_2 is more critical for C_2 lamps. Therefore, the loss of hydrogen by permeation is also more critical. Again low temperature bulbs and short life lamps are more suitable for chlorine regenerative cycle lamps.

4.4 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

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5.0 THE TUNGSTEN FLUORINE LAMP

5.1 Mechanism and Conditions for the Fluorine Regenerative Cycle

Fluorine is the most active of all the halogens. The fluorine-tungsten cycle is dependent on the formation and decomposition of tungsten fluoride. The general form of the reaction is as follows:

Tungsten (W) + Atomic Fluoride (F) $\longrightarrow$ WF_x

$W + 6F \longrightarrow$ Tungsten Hexafluoride WF_6

$WF_6 \xrightarrow{> 2750°C} W + 6F$

Fluorine is the only element to react at room temperature with tungsten and carbon giving gaseous fluorides WF_6 and CF_4. When fluorine is present in the gas-filling of a lamp, the evaporated filament material reacts to give gaseous fluoride which undergoes thermal dissociation at the hot filament. The cycle can be maintained at any bulb temperature.

The dissociation of tungsten fluoride and the deposition of tungsten only occur at very high temperatures in the immediate vicinity of the hot filament. With other halogens, in particular iodine which is now used in the well-known iodine lamp, the deposition occurs at relatively low temperatures in the gas filling so that a cloud of atomic tungsten is formed round the filament. While this already has a positive effect, the situation is basically more favorable with fluorine.

In the usual temperature range for the burning temperature of tungsten lamps, WF_6 just begins to dissociate to an appreciable extent.

The dissociation of WF_6 varies more strongly with the temperature than does the vapor pressure of the tungsten. As a result, a temperature increase at some point on the filament will increase the deposition of tungsten due to dissociation faster than the evaporation. Tungsten will thus be transported to the hot spot until its temperature again becomes equal to the mean value for the filament.

Unlike the other halides, which are largely dissociated at much lower temperatures and where the temperature dependence of the dissociation is less than that of the vapor pressure of the corresponding filament material, the fluoride can thus serve to homogenize and keep constant the temperature and the form of the filament. (Theoretically)

Fig. 5. *a)* Tungsten wire whose right-hand side has been made much thinner by etching.
b) The same spot on the tungsten wire after burning for 15 minutes at 3000 °C in 500 torr argon + 2 torr WF_6.

Reactions involving fluorine hinders the burning out of hot filaments as a result of evaporation, and the blackening of the bulb of the lamp by the evaporated filament material. The fluorine incandescent lamp can therefore be used at filament temperatures not far below the melting point of tungsten.

5.2 EFFECT OF IMPURITIES IN THUNGSTEN FLUORINE LAMPS

Because of the delicate balance necessary in fluorine lamps, control of impurities is critical.

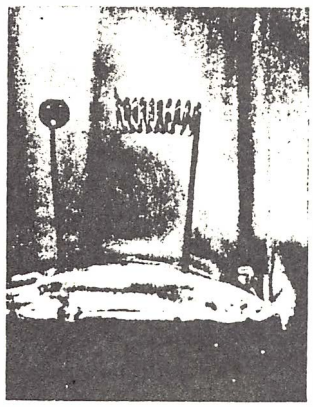
Metals such as nickel can form stable fluorides in cool regions and thus deplete the required supply of fluorine. The tungsten filament is the usual source of unwanted metals, and therefore its purity must be strictly controlled. Because the glass envelope of a halogen lamp is generally small, the operating temperature tends to be high; regions can range up to 1000°K or more. At such temperatures, it is common for hydroxyl radicals to be desorbed from the glass, particularly if Vycor with an hydroxyl content on the order of 100 ppm is used. The hydroxyl radicals

can form oxygen and thus disturb the required fluorine-oxygen balance. They can also form H_2O, and thereby introduce the well-known water cycle which accelerates the removal of tungsten from the filament.

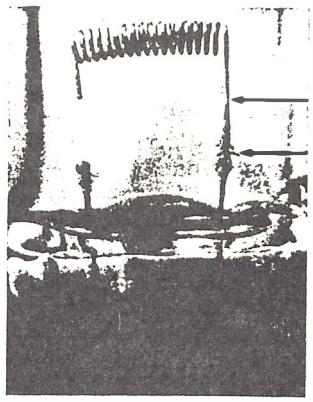
5.2.1 Effect of Oxygen on the Fluoride Cycle

For a general halogen cycle, an important consideration is the role of oxygen. In tungsten-iodine lamps the tungsten-bearing specie is WO_2I_2. In bromine lamps, it has been shown that WO_2Br_2 and $WOBr_4$ are relatively stable species. For a fluorine lamp, WO_2F_2 is the dominant specie at temperatures below 2500°K. All other tungsten-containing species have partial pressures lower by two orders of magnitude or more. Therefore, the cycle is really a tungsten-fluorine-oxygen cycle, and it is critical that both fluorine and oxygen be present in approximately equal amounts. If the F:O ratio deviates appreciably from 1:1, there are adverse effects on the cycle.

When F:O > 1:1, it is expected that tungsten will be transported to cool regions of the lamp. The filament legs and/or supports will be attacked.



F:O = 1:1



F:O > 1:1

When F:O < 1:1, the net effect is similar because the deposition of WO_2 will amount to undesirable net tungsten transport. For these reasons, the proper balance of fluorine and oxygen must be maintained.

5.3 Composition of Fluorine Addition to Fill-Gas

The attack on cool regions mentioned earlier suggests that the simple

addition of free fluorine to the usual inert fill gas (e.g., N_2, Ar or Kr) will not be satisfactory. Furthermore, fluorine by itself is very difficult to handle in manufacturing. Therefore, it would be preferable to use a fluorine compound which is stable and easily handled at normal temperatures, but which will decompose to liberate fluorine at the higher temperatures in the lamp.

Bromotrifluoromethane ($CBrF_3$) is a possibility, $CBrF_3$ does not decompose below about 550°C. In addition to fluorine, it can supply bromine for hydrogen gettering. It also supplied carbon which will be converted to CO which is stable above approximately 1250°C. Therefore, the carbon will act as an oxygen getter to help control F:O ratio.

The need to maintain the fluorine-oxygen balance indicates the need to perform manufacturing steps designed to eliminate impurities, including oxygen.

For example, filaments are heated to incandescence in hydrogen or forming gas (85% N and 15% H) to reduce any tungsten oxides. It is also common practice to heat the glass envelope while under vacuum to drive out hydroxyl radicals and thus prevent both H_2O and oxygen contamination. If the gettering of hydrogen by bromine is successful, then the deletion of these steps would leave oxygen as the only major impurity. However, oxygen is a necessary part of the fluorine cycle.

It should be noted that hydrogen and hydrides react particularly violently with fluorine. Fluorine even forms stable compounds with inert gases.

5.4 Lamp Performance of Lamps Made with $CBrF_3$

Experiment lamps have been made using normal lamp construction. That is a quartz bulb, Tungsten filament whose legs were welded to moly ribbons. Pt plating on moly ribbons was used as a weld flux.

There was no observable attack throughout the operating life of either the lamp walls or the filament legs near the walls for $CBrF_3$ concentrations up to 500 ppm. Therefore, there appeared to be no free fluorine (or HF) in the cooler regions.

Life was measured by operating the lamps at 14.00 $\pm$ 0.01 V DC, which produced a filament temperature of 3250°K. Life for a group of lamps with a fixed $CBrF_3$ concentration was determined by plotting time-to-failure on a Weibull plot. An example is shown in FIGURE 5.4.1 where the distribution has been approximately by a straight line. The intersection of the 50% failure point with this line is taken as the rated life. For the group of lamps in FIGURE 5.4.1, the fill gas contained 100 ppm of $CBrF_3$, and the life was 355 h. Life figures for other concentrations of $CBrF_3$ are listed in TABLE 1.. Note that higher and lower concentrations yield significantly lower life, indicating that the required fluorine-oxygen balance for lamps fabricated as described above occurs at $CBrF_3$ concentrations of~ 100 ppm.

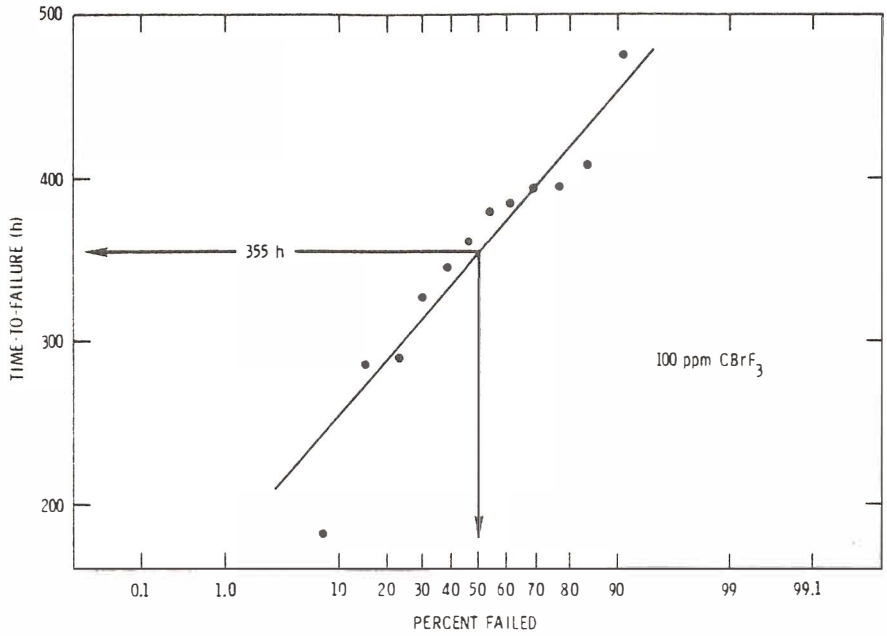


Figure 5.4.1

TABLE I. Average life at different $CBrF_3$ concentrations.

$CBrF_3$ concentration (ppm)	Life (h)
50	250
100	355
250	205
0[a]	140

[a] $CBrF_3$ replaced by CH_2Br_2;

$CBrF_3$ Replaced by CH_2Br_2

5.5 Reaction of Fluorine With Lamp and Equipment Construction Materials

Practically all materials normally used are attacked by fluorine. Glass reacts with fluorine and many flourine compounds, giving SiF_4. Organic materials like rubber, polyethylene, grease, etc., are attached by fluorine, often violently. Many metals react with fluorine even at room temperature.

Quartz glass is not attacked by fluorine under normal conditions, but at high temperatures or in the presence of water or organic compounds it is strongly attacked. Sintered corundum is very resistant, and calcium-fluoride ceramics can be used up to 900°C. Apart from platiumum a number of metals such as nickel, copper and aluminum are resistant to fluorine, because they become covered with a protective layer of fluoride. Silver-soldered connections must be protected by thick nickel-plating. Organic materials suitable for vessels and seals are polymeric tetrafluoroethylene and monochlorotrifluoroethylene. Low-polymer monochlorotrifluorethylene is a fluorine- resistant grease for taps, ground joints, etc. In TABLE I are given for a for a number of important materials the temperatures up to which they are not noticeably attached by fluorine.

TABLE 1. A number of fluorine-resistant materials. T is the limiting temperature up to which no noticeable attack occurs.

Material	T°C	Material	T°C
Platinum	300	Quartz	100
Copper	350	Polytetra-	
Monel	400	fluoroethylene	100
Magnesium	400	Corundum	700
Aluminum	450	CaF_2 ceramics	900
Nickel	500		

Fluorine reacts with nearly all elements and compounds at relatively low temperatures. Most metals, sulphur, boron, carbon, silicon and even asbestos react violently with fluorine at room temperature. Fluorine can displace the oxygen and halogen in halides and oxides, on gentle warming. Hydrogen and hydrides react particularly violently with fluorine. Fluorine even forms stable compounds with inert gases.

The great reactivity of fluorine is due on the one hand to the fact that fluorine forms the strongest known single bonds with other elements.

By way of example, TABLE II gives the dissociation energies of HX compounds (X signifies halogen) and the mean bond energies of CX and six molecules.

TABLE II. Dissociation energies and mean bond energies at 291°F in kcal/mole of fluorides compared with other halides

Dissociation Energies		Mean Bond Energies			
H-F	136	CF	110.0	Si-F	132
H-Cl	102.1	C-Cl	67.0	Si-Cl	86
H-Br	85.9	C-Br	54.5	Si-Br	69

The other factor determining the great reactivity is the surprisingly low dissociation energy of the molecule, viz 37.4 kcal/mole, compared to 118 kcal/mole for O_2, or 57.2 kcal/mole for Cl_2. The dissociation of F_2 already begins to be appreciable at 400°C and its degree of dissociation is greater than that of Cl_2, Br_2 and O_2 at comparable temperatures. A further reason for the aggressive behavior of fluorine may also be the high diffusion rate of the relatively small molecules and atoms.

Some fluorine compounds have a polar character. For example, the low-valency fluorine compounds of the metals are more strongly polar than the other halides. The lattice energies of the fluorides resemble those of the oxides more than those of the other halides. The fluoride ion can replace oxygen or the isoelectronic OH group in may structures. While e.g. $AlCl_3$ is a largely covalent compound, subliming as low as 180°C, AlF_3 is a non-volatile salt (melting point 1290°C). The bond in the HF molecule is also more strongly polar than that in the other hydrogen halides. The proton cannot penetrate far into the electron shell of the fluorine, giving a high dipole moment (1.91 debye). While the other halogen acids are monomeric and very volatile (boiling point of HCl = - 83.7°C), hydrogen fluoride (b.p. = 19.5°C) is polymerized by means of hydrogen bonds to chains and rings of low volatility.

The F-H-F bond is the strongest known hydrogen bridge. The enthalpy of formation for the reaction $HF + F \longrightarrow HF_2^-$ is about 50 kcal/mole, and for the reaction $2HF \longrightarrow H_2F_2$ is about 20 kcal/mole.

The fluorides of the non-metals and the high-valency transition metals, on the other hand, are typical covalent compounds. The dividing line between the salt-like and volatile fluorine compounds, runs diagonally through the periodic table from beryllium via aluminum, titanium and tin to bismuth. The molecules are the more volatile the more completely the central atom is surrounded by fluorine: thus the volatility increases with increasing valency. For example, WF_6 (molecular weight 297.92: b.p. = 17.5°C) is the heaviest known gas, and the fluorocarbons are more volatile than the hydrocarbons of the same molecular weight. The screening effect of fluorine is so strong that in molecules well surrounded by fluorine the weak intermolecular forces are comparable to those in the noble gases (see TABLE III).

TABLE III. Boiling point in °C of fluorides compared to that of chlorides, hydrocarbons and noble gases of comparable molecular weight.

	SF_6	C_2F_6	$C_{10}H_{22}$	CCl_4	Xe
Molecular weight	146	138	142.3	153.8	131.3
Boiling Point	-64	-78.3	+147	+76.8	-112

Some fluorides, e.g., SF_6, NF_3, CF_4 and higher homologues, also resemble the noble gases in their chemical behavior, and are completely inert up to moderate temperatures.

A particular feature of fluorine compounds is their very high heat of formation and thermal stability compared to all other compounds.

5.6 GLASS COATING TO RESIST THE ATTACK OF FLUORINE

It has been claimed that at least part of the attack of the envelope and mount is due to tungsten fluorides as well as free fluoride. This attack can be eliminated by coating the glass and mount with a metal phosphate or arsenate glass.

A liquid coating composition containing the metal phosphate or arsenate is dispensed from a hypodermic syringe through the lamp exhaust tube by inserting the needle of the syringe, discharging the liquid composition and then almost immediately drawing it back into the syringe, leaving only a thin layer adhering to the inside surfaces of the lamp structure. At this stage, the lamp is inverted to drain, and then heated in a vacuum or suitably inert atmosphere, for example at approximately 100°C for an hour in the case of a methanolic composition. The metal phosphate glass coating is finally formed by baking at a higher temperature, for example at 300°-500°C in a vacuum or suitable inert atmosphere for about 3 minutes in the case of an aluminum titanium phosphate composition. The final bake can be effectively incorporated in subsequent lamp processing.

The initial heating cycle is chosen to substantially remove the solvent and the time, temperature and atmosphere will depend upon the solvent selected. The temperature of the subsequent bake depends on the particular formulation used, but will in general be below 1000°C.

EXAMPLE

A liquid aluminum titanium phosphate coating composition was prepared by dissolving anhydrous aluminum chloride (1.946 g.) in methanol (992.467 g.) and pouring the solution into titanium tetrachloride (3.961 g.). Orthophosphoric acid (1.626 g.) was added to the resultant solution.

A tungsten filament lamp assembly was coated internally with this composition by the technique described above and the coated assembly thoroughly drained, heated at 100°C in vacuo for 1 hour, and baked at 400°C for 3 minutes also in vacuo. The lamp was subsequently filled with 3 1/2 atm. argon and 4 Torr WF_6 and finished in the usual way.

In operation, the lamp was successfully run at a filament temperature of 3000°C for 25 hours, and the failure at that time was not due to a breakdown of the coating. In contrast, similar lamps without the coating of this invention showed extremely rapid loss of fluorine due to reaction with the lamp components and had a life which in no case exceed 2 - 3 minutes.

5.7 INCANDESCENT FLUORINE CYCLE LAMPS

At this time (1980), there are no known production lamps using the fluorine cycle. What experimental work GTE Sylvania has done was related to the 1500 Watt linear lamps. The dose was fluorine (Freon) and oxygen. Lamp results were better than expected from the literature. No attack of the quartz was noted after 100 hours of lamp operation. The work was done at Boston Street, Salem, by Jim Keenan and D. Dayton.

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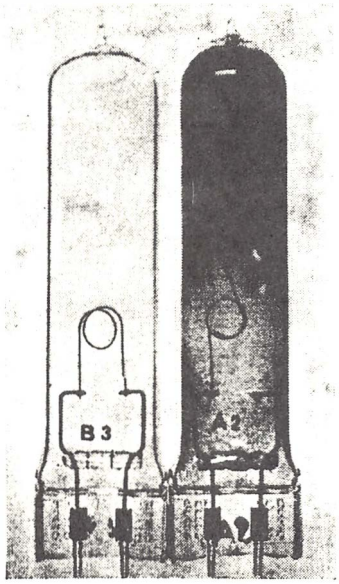
6.0 THE CARBON-FLUORINE LAMP

NOTE: The following is quoted directly from an N. V. Philips paper by W. J. Van Den Hoek.

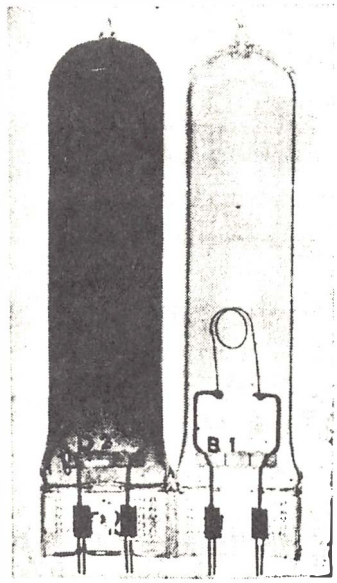
CARBON-FLUORINE LAMPS

The blackening behavior of experimental carbon-fluorine lamps appears to be in accordance with the theoretical predictions. Figures 13 and 14 give the results of some representative lamp experiments. Gas fillings and filament temperatures are given in TABLE IV . The gas filling of Lamp I and III is such that the constituent pressure has a value between 10^{-2} and 10^{-3} atm. The gas filling of IV is such that the constituent pressure is in the range above 10^{-1} atm. The results of lamps I and II need no further comment. Comparison of lamps III and IV shows the effect of the fluorine filling pressure.



I II

Fig. 13. The blackening in experimental lamps: without fluorine (II) and with fluorine (I).



IV III

Fig. 14. The blackening in experimental lamps. The effect of too much fluorine.

TABLE IV

Experimental Carbon-Fluorine Lamps

	filling pressures *)	filament temperature	lifetime
I	1 Torr CF_4		
	499 Torr Xe	2750 K	6 hr.
II	500 Torr Xe	2750 K	6 hr.
III	1 Torr CF_4		
	499 Torr Xe	2560 K	50 hr.
IV	100 Torr CF_4		
	400 Torr Xe	2560 K	2 min.

*) At room temperature

The present experiments clearly reveal the possibility of a carbon-fluorine cycle as predicted from the thermodynamic model. Even the critical dosage of fluorine appears to exist. Further systematic experiments indicated that a dosage of 1 Torr CF_4 is appropriate for filament temperatures in the range 2500-2800 K. At higher temperatures blackening occurs. The lifetimes*) over the indicated temperature range varied from about 50 to 5 hours. For the temperature range from 2800 to 3100 K a filling of 10 Torr CF_4 appeared appropriate. At 3100 K a lifetime of one hour was reached with a clear bulb wall.

A few other points call for comment in connection with the carbon-fluorine cycle.

i. The presence of a transport process is also evident from the behavior of the voltage or the current with time. In constant DC operation the voltage remained constant during most of the life of lamps filled with carbontetrafluoride. (The same applies to lamps with hydrogen or chlorine as the reactive gas, see below.) Lamps with only inert gas exhibit the usual increase of voltage with time, due to the evaporation of carbon.

ii. During the transport process various crystal growth phenomena occur at the filament. Some of these depositions are typical growth phenomena for carbon, in particular for pyrolytic graphite. Furthermore there are crystal growths due to the interaction of fluorine with the tungsten

supports. This results in the deposition of on the filament of mainly a - WC crystals and to a less extent B-WC_{1-x} crystals. Crystal depositions were identified by X-ray powder diffraction. This tungsten transport is in keeping with the thermodynamics of the tungsten-fluorine system as discussed by Dittmer et al. Nor is any blackening observed when the tungsten supports are coated with a carbon layer. This indicates that tungsten-fluorine reactions are not involved in the carbon-fluorine transport cycle that results in clear bulb walls.

iii. The use of transport reactions involving fluorine in quartz envelopes is problematical because of the reaction of SiO_2 with fluorine or fluoring-containing species. In general fluorine-resistant coatings should be used (e.g., by covering the wall with NiF_2, CoF_2 or fluorine-resistant glasses. In the present lamps no wall protection was applied. To discuss this question, we consider the equilibrium:

$$SiO_2(s) + CF_4(g) \rightleftharpoons SiF_4(g) + CO_2(g).$$

At 500 K the value of $\Delta G°$**) amounts to --64.2 kcal/mole. The equilibrium is shifted completely towards the right. For molecular halides, like carbon-fluorine compounds, however, it is known that if the bonding attains maximum covalency the compound becomes quite slow in its readtions. If CF_4 is brought into contact with quartz for times of the order of 0.5 s an observable reaction starts at 100°C.

The design of our experimental lamp is based on these considerations. The dimensions of the lamp are such that there is a sufficient distance (and thus a long enough convection path) between the hot gas zone around the filament and the wall. Consequently, the wall-temperature is low (500-600 K). On the basis of the partial-pressure curves given in Fig. 9a , it may be expected that mainly CF_4 molecules reach the wall. In this way, wall corrosion is prevented sufficiently for performing lamp experiments on a reasonable time scale.

If SiO_2 is dissolved in the gas phase the active fluorine content of the lamp is depleted, because the fluorine is gettered preferentially by Si. Experiments in small envelopes (i.e., of the type normally used for tungsten-halogen lamps) resulted in black walls. In these lamps, therefore, a fluorine protective coating should be used.

7.0 CARBON CHLORINE LAMPS

The behavior of carbon-chlorine lamps appears also to be in keeping wit- the theoretical expectations. See TABLE V . The argon-chlorine filled lamp (V) remains clear, while the reference, inert gas filled lamp (VI), blackens. Chlorine was introduced in the form of CCl_4. As stated in the experimental section, the presence of tungsten and any other metal should be avoided inside carbon-chlorine lamps. Tungsten-chlorine transport reactions result in the fast deposition of crystals of tungsten and various tungsten carbides on the filament. FIGURE VI gives a scanning-electron photomicrograph of these depositions on the filament almost immediately after the start of the incandescence. The transport is in keeping with the thermodynamics of the tungsten-chlorine system. The tungsten-chlorine transport reactions proceed much faster than the analogous fluorine reactions. This would be attributable to kinetic impedance if molecules such as CH_4 are involved.

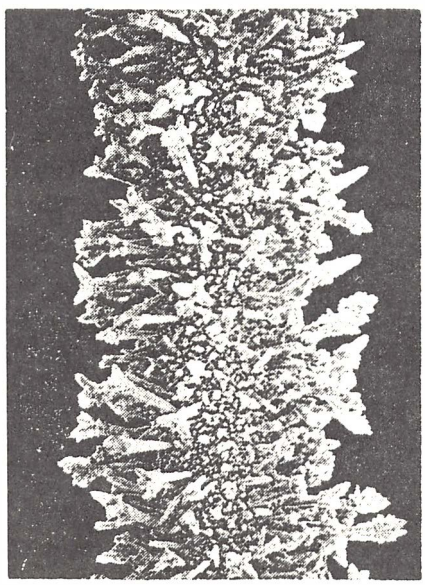


FIGURE VI . Tungsten and various tungsten carbides deposited on a carbon filament in a carbon-chlorine lamp. Filament temperature 2800 K. The diameter of the filament amounts to 237 µm.

TABLE V

Experimental Carbon-Hydrogen and Carbon-Chlorine Lamps

	Filling Pressures*)	Filament Temperature	Lifetime	Blackening
I	500 Torr Ar			
	0.1 Torr H_2	2800 K	330 min.	clear
II	500 Torr Ar	2800	64	black
III	500 Torr Ar			
	0.1 Torr H_2	3000	40	clear
IV	500 Torr Ar	3000	7	black
V	500 Torr Ar			
	1 Torr CCl_4	2800	200	clear
VI	500 Torr Ar	2800	130	black

*) At room temperature

Chemical transport studies indicate a possibility of improving the present carbon-vacuum lamp to a level corresponding to filament temperatures of about 2500 K. This may be brought about by using fluorine, hydrogen or chlorine in combination with an inert gas.

The experiments on the carbon-fluorine system indicate prospects for carbon-filament lamps with filament temperatures in the range from 2500 to 3000 K, provided that the lifetime can be increased by using well-graphitized carbon filaments, that appropriate wall-protection is present and that the lamp technology is adequate to avoid metals inside the lamp. The filaments used in our experimental lamps are inferior from the viewpoint of graphitization. Nevertheless in the temperature range 2500-3000 K, lifetimes varying from 50 hours to several hours were obtained.

8.0 FILL GAS FOR HALOGEN LAMPS

The purpose of the fill gas in a halogen lamp is to retard evaporation of the tungsten filament and to supply the small amount of halogen additive necessary for the operation of the halogen regenerative cycle. The selection of the fill gas and the halogen dose can be considered separately.

The laws governing tungsten evaporation as a function of temperatures are modified by the presence of the fill gas. The activity of the gas, its molecular structure, molecular weight, pressure, impurity content, as well as filament geometry, filament position and thermal currents are among the most important parameters to be considered.

The gases commonly used for halogen lamp filling include:

N_2	Nitrogen	100%	High Volt Projection Lamp
Ar	Argon	100%	Double Ended Lamps
Kr	Krypton	100%	High Efficiency Projection and Automatic Lamps
Xe	Senon	100%	Maximum Efficiency Special Lamps

With the exception of Nitrogen, the filling gas is usually a mixture of N_2 and Argon, Krypton or Xenon.

8.1 Carrier or Fill Gas

The following table shows the fill gases for common halogen lamps as a function of lamp wattage and volts.

Voltage	Wattage	Type of Fill Gas
0-65	0-250	N_2 or Ar or Kr (or any combination of same)
0-65	> 250	N_2 or Ar (or Ar + N_2)
65-90	0-650	N_2 or Ar + N_2 or Kr + N_2
65-90	> 650	N_2 or Ar + N_2
90-120	0-650	N_2 or Ar + N_2 or Kr + N_2
90-120	>650-760	N_2 or Ar + N_2
90-120	> 750	N_2
> 120	All Values	N_2

The coil length is also a consideration when selecting fill gases. The following table shows fill gases as a function of lamp wattage, volts and coil length.

Voltage	Wattage	Coil length(mm)	Type of Fill Gas
0-90	0-250	0-50	N_2 or Ar (or Ar + N_2)
0-90	0-250	50	N_2 or Ar or Kr (or any combination)
0-90	> 250	All values	N_2 or Ar (or Ar + N_2)
> 90	All values	All Values	N_2 or Ar or Kr + N_2 (or Ar + N_2)

If volts/mm has a high value (e.g., 100 volts/mm) then N_2 must definitely be used. In fact, if in doubt use N_2.

8.2 Selecting a Fill Gas

The filling gas is chosen to provide a balance between suppression of evaporation of the filament and arcing (flashover between leads). The ability to suppress filament evaporation increases with molecular weight.

Table 8.2.1 shows important properties of fill gases.

TABLE 8.2.1

	Nitrogen	Argon	Hydrogen	Krypton	Xenon
Chemical Symbon	N_2	Ar	H_2	Kr	Xe
Molecular Weight	28.016	39.944	2.016	83.70	131.3
Specific Gravity Air=1(70°F.1 Atm)	0.9670	1.380	0.06950	2.894	4.560
Density (70°F 1 Atm)	.07247	.1034	.005209	.2169	.3417
NORMAL °F	-320.45	-302.55	-423.0	-243.81	-162.51
BOILING °C	-195.8	-185.7	-252.7	-151.8	-109.1
POINT °K	77.3	87.4	20.4	121.3	164.0
Breakdown Voltage Approx.	2500	250		420	500

Pure N_2 has a flashover potential ten times higher than pure Argon but heat losses by conduction through Nitrogen would be high and the reduction of W evaporation would be less in N_2. A mixture of N_2 + Ar, K, or Xe is necessary. The N_2 should be kept to a minimum. It is not possible to calculate the flashover voltage of a mixture from the physical characteristic of its components. Flashover is also suppressed by additions of H_2, H_2O vapor and fill pressure. The higher the pressure in lamp the more resistance to arcing.

8.2.1 Selection of Fill Gas for Tipping Method

The usual method of tipping halogen lamps is to freeze out the fill gas and halogen additive and tip as a vacuum lamp. Of course, in the case of nitrogen, there is no freeze out but there is pressure reduction by temperature.

$$T_2P_1 = P_2T_1$$

where T_1 = Temperature of gas at fill in °K

T_2 = Temperature of liquid nitrogen in °K

P_1 = Fill Pressure

P_2 = Tipoff Pressure

The following table shows the approximate pressure in a lamp just befor tipping at liquid nitrogen temperatures.

Argon	201 Torr
Krypton	5 Torr
Oxygen	162 Torr
Nitrogen	760 Torr

100% Krypton lamps sometimes become contaminated by water vapor, oxygen, etc. due to the lamp acting as a cryogenic pump wherein the gases in head and sweeps are sucked back into the lamp becuase of the low pressure in lamp. The collected gases condense in the lamp and remain there during tipoff. The problem is often observed visually by a white cast on the bulb. The problem can be eliminated by mixing a small amount of nitrogen with the Krypton. The nitrogen addition will not freeze out and will be left when the Krypton freezes out. The amount of nitrogen added should be as little as necessary to prevent the problem. The pressure in lamp at tip off varies with the partial pressure of N_2 added to the fill gas.

For a nitrogen filled lamp there is a limit to the fill pressure. Assuming a 650 Torr pressure at tipping and liquid nitrogen temperatures, the fill pressure will be as follows:

$$T_2P_1 = P_2T_1$$

$$P_1 = \frac{P_2T_1}{T_2} \qquad \begin{aligned} P_1 &= X \\ P_2 &= 650 \\ T_2 &= 77°K \\ T_1 &= 298°K \end{aligned}$$

$$P_1 = \frac{650 \times 298}{77}$$

P_1 = 2515 Torr = 3.3 atmosphere absolute

8.2.2 Lamp Fill Pressure

The room temperature fill pressure is dictated by the fill gas and tipping method. The following table shows accepted fill gas pressure range.

Type of Fill Gas	Pressure (atmospheres)
N_2	1-3 (see note 1)
Ar or Kr	1-10 (see note 2)
Any combination of inert gas	1-10 (see note 2)

Note 1: Limited by practical difficulties encountered during tipping.

Note 2: Only limited by the strength of the press seal or envelope.

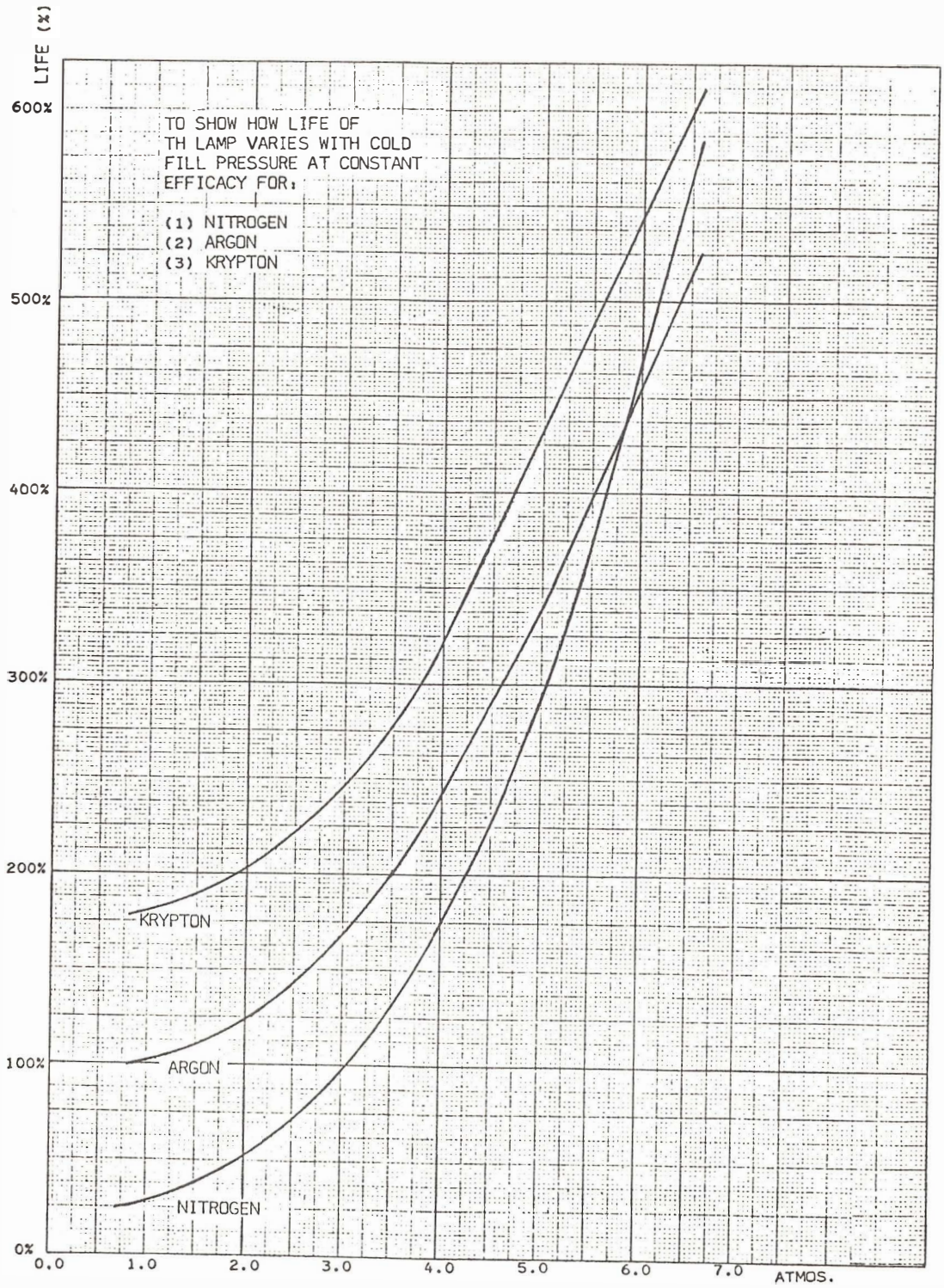
8.3 Evaporation Rate and Life as a Function of Fill Gas

The evaporation rate of incandenscent W filaments with pure Kr is only 60% of that with pure Ar and is even lower with Xe. Kr and Xe are much more expensive than Ar and are only used for special lamps. The mixing of the pure gas with various amounts of N_2 increases the evaporation rate of W.

8.4 Effect of Fill Gas Pressure

Both arc suppression and evaporation rate are improved by increased pressure. The evaporation rate at a given filament temperature varies inversely with the pressure. Double the pressure reduces evaporation rate by a factor of two and thus doubles the life of the lamp. Pressure is limited by bulb geometry, bulb size, and application. G.L.S. lamps are filled to a little less than atmospheric and in operation the internal pressure is atmospheric or a little above. Some small quartz lamps run at ten atmospheres or more.

The general rule of double pressure means double life is only approximate and varies with the fill gas and mixtures. The following graphs show more accurate data based on actual experience where lamp failures are influenced by factors in addition to evaporation. The shorter the rated lamp life, the more likely the lamp will fail due to classic evaporation.


LIFE (%)
600%
500%
400%
300%
200%
100%
0%
TO SHOW HOW LIFE OF
TH LAMP VARIES WITH COLD
FILL PRESSURE AT CONSTANT
EFFICACY FOR:
(1) NITROGEN
(2) ARGON
(3) KRYPTON
KRYPTON
ARGON
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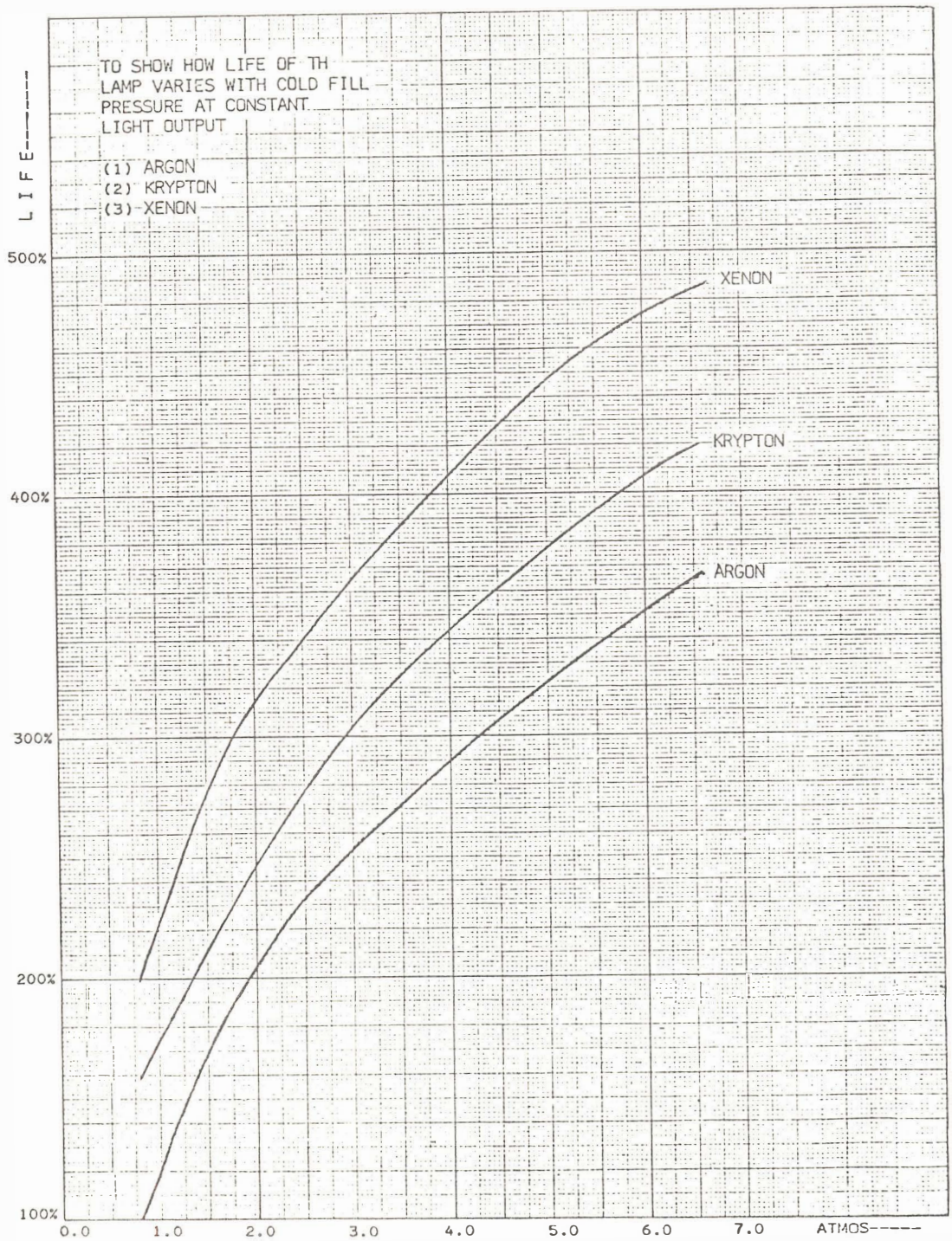
TO SHOW HOW LIFE OF TH
LAMP VARIES WITH COLD FILL
PRESSURE AT CONSTANT
LIGHT OUTPUT
(1) ARGON
(2) KRYPTON
(3) XENON
L I F E
500%
400%
300%
200%
100%
XENON
KRYPTON
ARGON
0.0
1.0
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3.0
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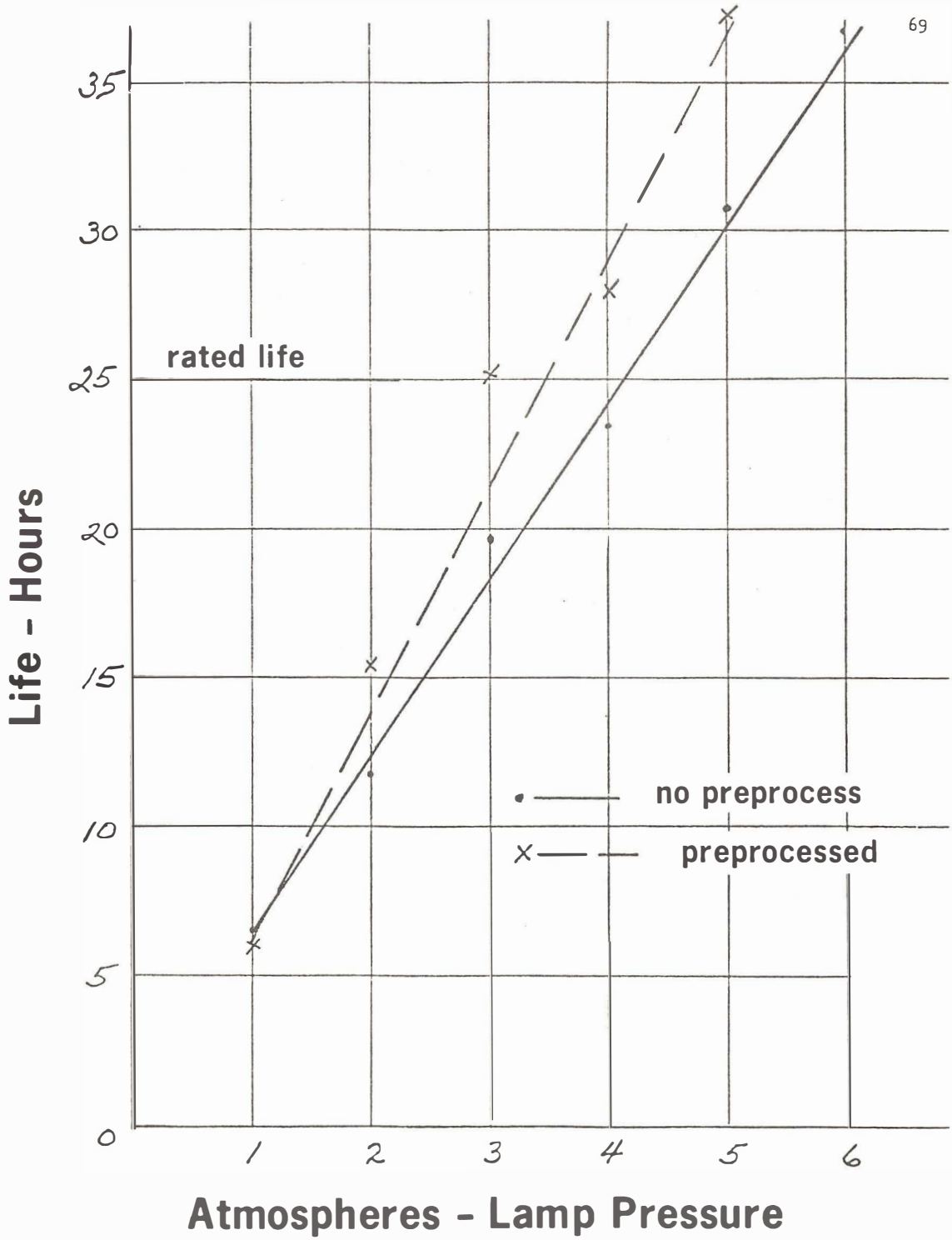
5.0
6.0
7.0
ATMOS


69
35
30
25
20
15
10
5
0
rated life
Life - Hours
no preprocess
preprocessed
1
2
3
4
5
6
Atmospheres - Lamp Pressure

8.5 Thermal Conductivity of Fill Gases

The thermal conductivity of the filling gas varies with its molecular weight. The thermal conductivity also varies with the fill gas pressure. Table 8.5.1 shows the thermal conduction of fill gases as a function of the temperature.

TABLE 8.5.1

Thermal Conduction, σ, Expressed in Watts Per Cm for Various Gases

T, °K	N_2	A	Kr	Xe
0	0	0	0	0
200	0.017	0.013	0.007	0.004
400	0.064	0.048	0.025	0.015
600	0.133	0.100	0.053	0.031
800	0.288	0.166	0.089	0.052
1000	0.345	0.245	0.132	0.077
1200	0.485	0.336	0.184	0.108
1400	0.650	0.437	0.243	0.143
1600	0.839	0.551	0.309	0.182
1800	1.055	0.674	0.380	0.225
2000	1.291	0.811	0.459	0.271
2200	1.548	0.960	0.544	0.322
2400	1.825	1.119	0.634	0.375
2600	2.126	1.288	0.728	0.431
2800	2.447	1.469	0.828	0.491
3000	2.787	1.660	0.932	0.553
3200	3.154	1.856	1.039	0.617
3400	3.539	2.068	1.153	0.685

8.6 Mixing Fill Gases

The mixing of gases also affects the ternal conductivity of the fill gas.

Fill Gas	Relative Thermal Loss
N_2 100% (570 Torr)	498
87 Ar + 13% N_2 (570 Torr)	392
87 Kr + 13% N_2 (570 Torr)	301
Ar 100% (570 Torr)	299
Kr 100% (570 Torr)	169
Xe 100% (570 Torr)	100

8.6.1 Light Fill Gases vs Heavy Fill Gases

The net result of gas filling with heavier gases is as follows:

	Light Gas	Heavy Gas
Gas Cost	Low	High
Bulb Size	Big	Small
Lamp Efficiency (Lpw)	Low	High
Lamp Life	Low	High
Bulb Temperature	High	Low
Flashover Voltage	High	Low

In commercial G.L.S. coiled coil lamps with Kr/N_2 (600 Torr) fillings, the light yield is 4-11% higher than Ar/N_2 (90/10) filled lamps of equal rating. Xenon fillings gives three times the life of Kr filled lamps of same Lpw or 17% more light at the same life. Halogen Lamps would be expected to behave much like GLS lamps as long as the failure mechanism of both was filament evaporation.

Gas	Relative Evaporation	Relative Lamp Life
Vacuum	100%	1.0 Hour
N_2 100% (600 Torr)	4%	25 Hour
86 Ar + 14 N_2 (600 Torr)	2.5%	40 Hour
Ar 100% (600 Torr)	2%	50 Hour
Kr 100% (600 Torr)	1.2%	83 Hour
Xe 100% (600 Torr)	1.0%	100 Hour

Argon, Krypton and Xenon gas can be obtained as pure gas (99.99%) or as a mixture with pure nitrogen used as a diluent to obtain any desired degree of purity.

The evaporation rate varies in Ar/N_2 mixtures as a function of the N_2 content. Lamp life varies with the evaporation rate.

Mixture		Relative Evaporation	Relative Lamp Life
Ar	N_2		
100	0	100	100 Hours
98	2	100.85	98.15 Hours
96	4	103.79	96.21 Hours
92	8	107.76	92.24 Hours
90	10	109.77	90.23 Hours
88	12	111.80	88.20 Hours
86	14	113.83	86.17 Hours

8.7 Effect of Contaminants in Fill Gas on Lamp Performance

The purity of the fill gas is a major factor in lamp life. The impurities usually react chemically with the filament.

Halogen lamps react similarly to any gas filled lamp, that is, halogen lamps are prone to water cycles, brittle filaments from carbon, filament sag due to oxygen, oxygen cycle due to CO_2/CO ratio, etc. The difference is that a small amount of oxygen in the form of CO is needed and hydrogen is needed to act as a buffer on any free halogen except iodine in the lamp. Otherwise, the bromine, chlorine or fluorine will attack the legs of coil and leads.

8.7.1 Oxygen

Oxygen is probably the most common impurity left in lamps after exhaust and, because its action is more moderate than that of some of the other impurities, slight traces may show no apparent damage. Oxygen combines readily with tungsten at red heat, and more rapidly as temperature increases. The oxides formed at the hot filament volatilize and are carried by the gas stream to the bulb walls and other cooler parts of the lamp, where they condense to produce their characteristic deposits.

The composition of the oxides formed, and the appearance of the deposit produced will vary with the amount of oxygen present and the temperature at which they are formed. An 0.2% mixture of oxygen in the lamp atmosphere will produce a thick yellowish-white deposit of tungsten oxide (WO_3) which covers the interior of the lamp. With lower percentages of oxygen, the color of the oxide being produced will vary from white to light blue and finally dark blue. With these smaller amounts of oxygen, the deposit on the bulb wall or lead tips may appear as a brown or black color which can be confused with the discoloration caused by other impurities.

The action between the tungsten filament and oxygen (by itself) will occur at initial light-up and this action becomes complete as soon as the oxygen is used up. No further discoloration, other than some white to blue deposit on bulb due to the evaporated tungsten, should therefore

occur throughout the life of the lamp, unless the lamp is a leaker and additional oxygen is introduced through breathing-in of atmospheric air.

The oxide deposit produced by slight traces of oxygen in the atmosphere of lamps having a large bulb surface may therefore not be readily apparent and cause no appreciable loss in light output. However, the attack of the oxygen on the tungsten may be localized at certain critical temperature points along the filament to produce hot spots which can cause shortening of lamp life. Moreover, if hydrogen is also present by degassing from glass and metal parts or from the halogen dose, it can react with the tungsten oxide deposits producing water and the destructive water cycle.

8.7.2 Water Vapor

Water vapor is one of the more stubborn impurities to remove from the lamp during the exhaust process. If present in the finished lamp atmosphere, its effect on lamp performance is similar to that of oxygen but considerably more vicious in that it has a recurring action commonly known as the water cycle.

Water vapor in the region of the hot filament, becomes dissociated into its elements - hydrogen and oxygen. The free oxygen readily combines with the hot tungsten, to form tungsten oxide, which volatilizes and is carried away by the gas stream to be deposited in the cooler areas of the lamp interior. The intense heat of the filament also causes the molecular hydrogn to dissociate into hydrogen atoms. The hydrogen, in this very active state, is able to reduce the tungsten oxide to leave metallic tungsten which would appear as a grey or black deposit on the bulb wall if it was not removed by the halogen cycle and redeposited on the filament.

The reaction, in which the tungsten oxide is reduced, simultaneously recreates water vapor which will again attack the hot filament and this repeating cycle will go on unhampered throughout the life of the lamp. Lamps containing only a trace of water vapor will show abnormal growth or faceting early in lamp life but the faceting will also continue to

progress at a more rapid rate than that due to the normal evaporation of tungsten from the incandescent filament.

In addition, the attack on the tungsten usually occurs at certain critical temperature points along the filament.

This results in necking down of the wire to form hot spots and cause early burnout. The thinner spots of the filament will also have much reduced shock resistance. In addition, there may be arcing between turns due to spikes built up by the redeposited tungsten.

8.7.3 Carbon and Carbon Compounds

Carbon as a single impurity in a lamp does not cause life problems but can produce brittleness and distortion of the tungsten filament.

Hydrocarbons, in the form of oil vapors, can be carried into the lamps during the exhaust process, if the machine lines are not kept clean. Such hydrocarbons will dissociate, at filament operating temperatures, and react with the hot tungsten to form carbides and produce the brittleness and squirm. In addition, some of the carbon will deposit on the bulb wall resulting in a drop in light output. In addition, the freed hydrogen, in the presence of oxygen, sets the stage for the water cycle which will continue to cause abnormal thinning of the filament wire in the first turn area throughout the life of the lamp. The oxides of carbon (CO and CO_2) also can produce tungsten cycling. Carbon dioxide can dissociate in the higher temperature regions of the lamp, to form carbon monoxide and oxygen. There are also several reactions which can occur between carbon monoxide and the tungsten, depending upon the temperature conditions. In addition, because of the temperature gradients in the lamps, these reactions become reversible to produce a cycling condition in which the tungsten is gradually removed from portions of the filament and build up on other portions of the filament. The roll of carbon in preventing high temperature sag is discussed in Section 13.8 Filament Sag Control.

8.8 Methods of Purifying Lamp Fill Gases

In most new lamp plants, N_2 and Ar are purchased as liquids and then evaporated and mixed to make lamp gases. Gases from liquids are quite clean. Krypton is purchased in high pressure tanks. When the gas is passed through pipes, etc., the gas can become contaminated.

The following table shows the levels of contamination that should not be exceeded.

TABLE 8.8.1

Gas Purities	Filling or Flushing
Oxygen	< 5.0 PPM
Hydrogen	nil
Carbon Dioxide	< 0.5 PPM
Hydrocarbons	< 2.0 PPM
Water	< - 76°F dewpoint

NOTE: These values are readily attainable from liquid sources. System operation and maintenance must be rigidly controlled. Many installations need in-house purification especially for gases purchased in cylinders. Analysis equipment is recommended.

Purification of the gases can be at the source or at the exhaust machine. The best place is at the exhaust machine even though a purifier is needed at each machine instead of one purifier at the source.

Table 8.8.2 shows several absorber materials (getters) and the contaminants they will remove.

TABLE 8.8.2

Getter Capacities for Gases and Metals

Getter Material	Gas					
	CH_4	CO	CO_2	H_2	N_2	O_2
Ba	0	0.2	0.2	0	0	1
Sr	...	0.1	...	...	...	...
Mg	...	0	...	...	...	...
Mo	0	0.15	...	0.05	0.05	0.5
Ta	0	0.08	...	0.5	0.1	1
Ti	0	0.15	0.13	2	0.05	1

Centorr Co., of Suncook, New Hampshire, is a source of getter furnaces for fill gas purification. The absorber material is Ti. The furnace temperature is set at 650°C max. At this temperature, H_2, O_2 and H_2O vapor will be gettered. At higher temperatures, the getter material would getter N_2 and become saturated.

The removal of water vapor from the fill gas is the most important gettering operation.

Table 8.8.3 shows the effectiveness of various drying (water vapor gettering) materials.

TABLE 8.8.3

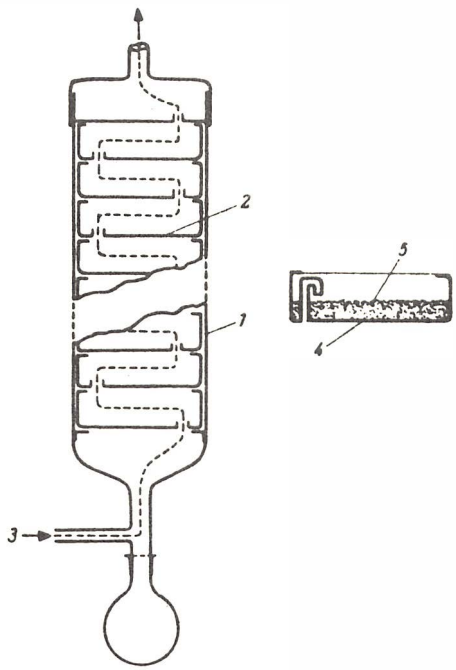
Efficiency of Drying Agents, Measured by Residual Water in mg/liter Gas After Drying at 25°C

Cold Filter at -180°C	10^{-16}
P_2O_5	$< 2 \times 10^{-5}$
$Mg(ClO_4)_2$	$< 5 \times 10^{-4}$
$Mg(ClO_4)_2 \times 3\ H_2O$	$< 2 \times 10^{-3}$
BaO	--
KOH (fused)	2×10^{-3}
Al_2O_3	3×10^{-3}
H_2SO_4	3×10^{-3}
MgO	8×10^{-3}
Silica gel	--
NaOh (fused)	1.6×10^{-1}
$CaBr_2$	2×10^{-1}
CaO	2×10^{-1}
$CaCl_2$ (granular)	1.4 to 2.5×10^{-1}
$CaCl_2$ (technical grade unhydrous	--
$CaCl_2$ (dehydrated at 250°C)	--
H_2SO_4 (95.1%)	3×10^{-1}
$ZnCl_2$	3×10^{-1}
$ZnBr_2$	1.1
$CuSO_4$	1.4

Flow rate about 100 m^3 air per hr per cm^3 drier. The most effective dryer is phosphorus pentoxide (P_2O_5). When a gas has been sufficiently

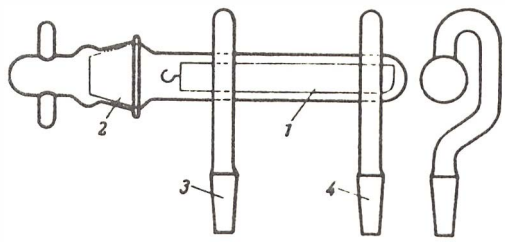
dried over P_2O_5 the vapor pressure of residual water is only about 3×10^{-7} Torr.

The apparatus to use P_2O_5 can take many forms.



Gas Drier with P_2O_5

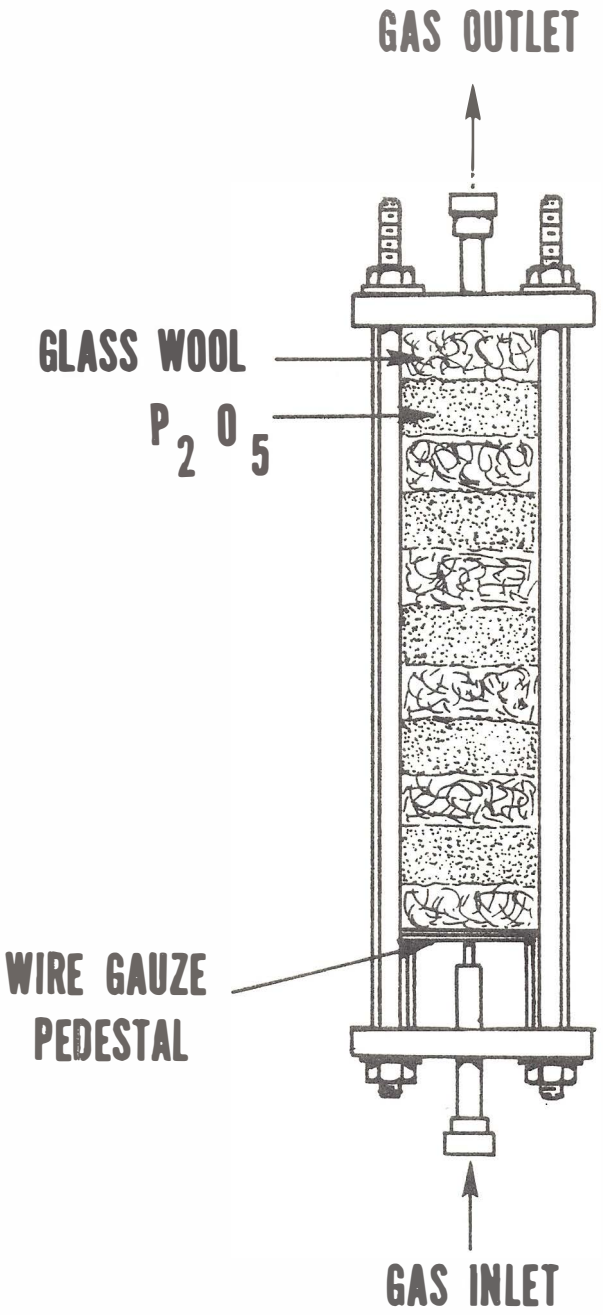
1 Stainless Steel Outer Tube; 2 Insert Plate Provided with Layer of P_2O_5 and Gas-entry Ports in the Sides; 3 Path of Gas When Being Dired; 4 Another Form of Insert Plate; 5 P_2O_5 Layer.



Gas Drier Made of Glass, with P_2O_5

1 Porcelain Boat with P_2O_5; 2 Filling Port with Ground-Glass Closure: 3 Inlet, and 4 Outlet for Gas to be dried: 3 and 4 have Standard Cones for Joining Gas Lines. The Right-Hand Illustration is an End-on View.

P_2O_5 used for drying must be free of As and lower oxides of P which would otherwise form volatile compounds with various gases and vapors; for example, water vapor reacts to form highly toxic phosphine (PH_3). They are removed by putting technical-grade material into a red-hot procelain dish and agitating in a stream of O_2. (Merck produces a phosphorus pentoxide grade properly purified for vacuum work, called Acid, phosphoric. anhydr. albiss. pro anal.) The drying agent is generally inserted in the gas line in a special container (porcelain or glass boat) through a glass port. It is also possible to fill large drying towers with about 500 g P_2O_5 and a number of glass tubes about 20-25 mm long, 15-20 mm dia;



IMMEDIATELY AFTER FILLING THE DRIER MUST BE PUMPED AND FILLED WITH ARGON AND THE ENDS PLUGGED-UP.

PHOSPHORUS PENTOXIDE (P_2O_5) DRIER USED IN GAS LINES ON PUMPING SYSTEMS

the whole unit is then shaken up thoroughly to distribute the drying agent throughout the tower. After about 100 hr operation, the tower is removed from the gas line and shaken again.

If the pentoxide has become sticky and of honey-like to gelatinous consistency, it should be removed by washing out in hot water and replaced by fresh. In large-scale driers, the drying agent can be placed on metal plates provided with side-holes and the plates stacked vertically in an Fe tube.

P_2O_5 drying bottles for lamp equipment are usually about 15 inches high and about 3 inches in diameter. The inlet is on one side near the bottom and the outlet on the opposite side near the top. The bottle is filled with glass stem flares, glass wool and P_2O_5 granuals such that the input gases must flow in a long path before reaching the outlet. These assemblies are made up in the chemical lab, at the lamp plant.

8.9 Testing Gas Purity

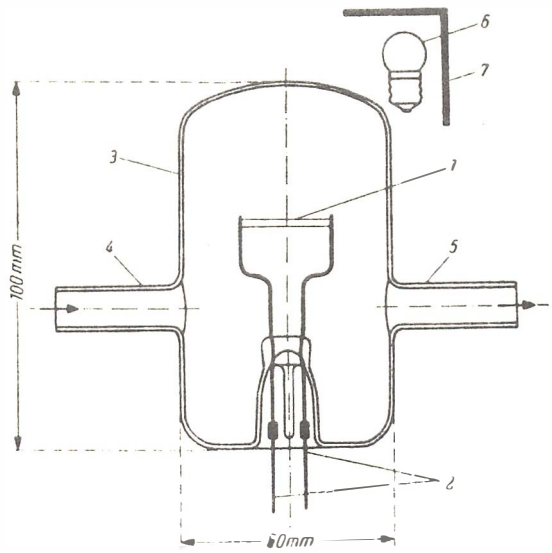
There are commercial devises for continuous recording of water vapor in protective gases, in particular water in H_2 for degassing furnaces; one example is the "Moisture Monitor Type 26-301" of the Consolidated Electrodynamics Corp., Pasadena, California, U.S.A. These can determine moisture concentrations over the range 1 to 1000 x 10^{-4}% of the test-gas volume, with reasonable response times; this amounts to dew-points of -76° to -20°C. They operate on the principle of simultaneous absorption and electrolysis of water vapor with the aid of an electrolytic cell. The cell consists of two mutually-insulated, closely-spaced Pt wires coated with a film of P_2O_5, and across which a voltage is applied so that measurement can be made of the electrolyte current produced by water absorption.

There are also commercial devices for continuous recording of O_2 in gases, for instance the "Super-sensitive Oxygen Indicator" Model SS-4S made by Baker & Co., Newark, New Jersey. U.S.A. The principle is

determination of the heat developed in a H_2--O_2 reaction on a noble-metal catalyst, and the concentration ranges from 2 to 200 x 10^{-4}% and 200 to 2000 x 10^{-4}% of the test-gas volume. The gas flow rate required is 114 liters/hr at 1 atm pressure.

A common lamp plant test is the "puff test." In this test, the gas is passed over a heated tungsten filament. The filament temperature is high enough to oxidize but not high enough to vaporize tungsten oxide (approx. 1300°C). Oxygen causes the normally bright tungsten to darken. The surface can be renewed by raising the filament temperature and evaporating the WO to condense on the bulb wall. The evaporation is seen as a "puff" of smoke.

Figure 8.9.1 shows a typical lamp plant device



Indicator Tube for Traces of O_2 in H_2, N_2 or inert gases

Figure 8.9.1

9.0 THE EXHAUST-FLUSH-FILL PROCESS

The term "exhaust," as used in lamp making, refers to the process of obtaining a favorable atmosphere in a lamp enclosure, which will permit the filament to be heated to incandescence to produce an efficient light source for a reasonably long time.

Basically, the primary function of lamp exhaust is the removal of atmospheric air and adsorbed gases from the bulb interior, including the bulb walls and mount parts. Heat is a necessary part of the exhaust process. It is responsible for freeing and adsorbed gases from the surface of the glass and metal parts. The heat may come from the sealing cycle or from an oven in the early part of the exhaust process.

9.1 Type C (Gas Filled)

The objective of the type C exhaust process, used for gas filled lamps, is to remove the atmospheric air and moisture from the lamp and introduce a dry inert gas plus the halogen dose which will serve as the final lamp atmosphere. This is accomplished by a repeated dilution, or rinsing process in which the original air is gradually reduced to a negligible amount and simultaneously replaced by the inert gas (usually an argon or Krypton nitrogen mixture). This process consists of an initial rough evacuation to remove the bulk of the air, followed by a series of cycles in which the lamp is alternately flushed and evacuated to controlled pressures, and then finally filled with the required filling gas.

This process does not require the use of a high vacuum source because, at no time, is it necessary to pump the lamp to a pressure below approximately 1 mm. In addition, the turbulence produced by the flush gas, as it rushes into and out of the lamp, tends to scrub the adsorbed films of moisture and other impurities from the internal glass and metal surfaces, and this dry gas also acts somewhat like a blotter to pick up the water vapor and aids in removing it.

The extent to which the original air can be removed from the lamp by this flush exhaust process is dependent upon several factors, including:

1. The pressure (P_I) to which the lamp is initially pumped,
2. The pressure (P_F) to which the lamp is flushed,
3. The pressure (P_V) to which the lamp is pumped after each flush, and
4. The number of times (n) the lamp is flushed.

These factors can be arranged into a simple formula which can be used to calculate the partial pressure of air (P_A) due to the original atmospheric air, remaining in the lamp after any number of flushes or with any combination of in-process pressures.

$$P_A = P_I \left(\frac{P_V}{P_F}\right)^n$$

All lamp pressures (P_I, P_V, and P_F) are in terms of mm Hg (absolute) and they represent actual pressures attained in the lamps at some common temperature. For convenience, these pressures are usually measured at room temperature and corrected to 20°C (77°F) to provide a common base for all measurements.

The partial pressure (P_A) of the residual air will also be expressed in terms of mm Hg at this same temperature, but it can be converted into the more common form, of parts-per-million (PPM) of the total gas in the finished lamp, by substituting the calculated value for P_A in the following expression.

$$\text{PPM (air)} = \left(\frac{P_A}{P_L}\right) \times 10^6$$

where P_L is the final lamp filling pressure (in mm of Hg.

The following table shows the same results can be obtained without pumping into a high vacuum:

Case I T-4 Bulb

1.	Pump to 10 Torr	PI = 10
2.	Flush to 100 Torr	PF = 100
3.	Pump to 10 Torr	PV = 10
4.	Repeat 2 & 3 four times	n = 4
5.	Fill to 600 Torr	PL = 650

$$\text{PPM (air)} = \frac{PI\left(\frac{PV}{PF}\right)^{n}}{PL} \times 10^{6}$$

$$= \frac{10X\left(\frac{10}{100}\right)^{4}}{650} \times 10^{6}$$

PPM (air) = 1.538

Case II. T-4 Bulb

1.	Pump to 1 Torr	PI = 1
2.	Flush to 1000 Torr	PF = 1000
3.	Pump to 100 Torr	PV = 100
4.	Repeat 2 & 3 three times	n = 3
5.	Fill to 650 Torr	PL = 650

$$\text{PPM (air)} = \frac{PI\left(\frac{PV}{PF}\right)^{n} \times 10^{6}}{PL} = 1\left(\frac{100}{1000}\right)^{3} \times 10^{6}$$

PPM air = 1.538

Note that in Case II, the initial pump down was lower but the flush pressure and pumps were higher and that only 3 flush pump cycles were used to equal 4 in Case I.

The use of high pressure flush and pump cycles results in much faster exhaust cycles. The following table shows the time to pump some standard lamps to various pressures. The fill pressure in all bulbs is 800 Torr and same size exhaust tube used.

LAMP PRESSURE

Time	A-19 (132 cc)	R-30 (287 cc)	R-40 (705 cc)	T-4 (6.43 cc)
.5 sec.	110	244	491	5.35
1.0 sec.	40	135	371	1.95
1.5 sec.	15	74	280	0.73
2.0 sec.	6	41	212	0.30

The table shows that for viscous pumping range (1000 Torr & down to 1 Torr) the pumping speed is much faster at higher pressure differential between lamp and pump manifold and, of course, the internal lamp volume is a factor. Halogen Lamps usually have small volumes.

Speed varies with $\frac{a}{l}^4$ and pressure differential, ΔP, where (a) is radius of exhaust tube, l is length of exhaust tube and ΔP is pressure in lamp minus pressure in pump manifold. The data shows that the time to pump from 100 Torr to 10 Torr in Case I is approximately (1.75 - .5 sec.) 1.25 seconds per cycle. With 4 cycles, 4 x 1.25 = 5 seconds. In Case II the time to pump from 1000 Torr to 100 Torr is approximately .5 seconds.

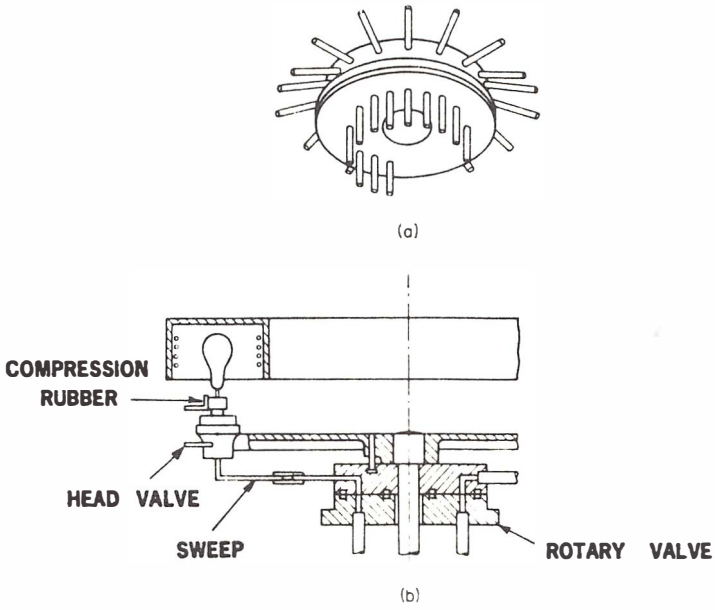
With 3 cycles, 3 x .5 = 1.5 seconds and even with an extra .5-1 sec. for initial pumping to 1 mm instead of 10, there is considerable pumping time saved. The following rules of thumb hold for processing gas filled lamps.

1. Heat bulb as hot as possible before exhaust either by sealing cycle or by oven on exhaust cycle. If oven is used, flush lamp to approx. 800 Torr after leak checking and do not pump until after maximum oven temperature is reached.
2. Pump to less than 5 Torr before first flush.
3. Flush to at least 760 Torr.
4. Pump to less than 100 Torr.
5. Allow at least 3 flush-pump cycles.
6. Pump to at least 1 Torr.
7. Fill to specified pressure.

The residual air should calculate to be less than 5 PPM. Values less than 1 PPM are not realistic because of inherent contaminants in the flush and fill gas.

9.2 The Exhaust-Flush-Fill Equipment

The exhaust machine is an indexing turret type machine. The sequence of operations required for applying the flush-exhaust process is controlled by a rotary valve located at the center of the machine. Figure 9.2.1 (a) is an external view of a complete valve. Figure 9.2.2 is a view of the inner surface of a typical valve.



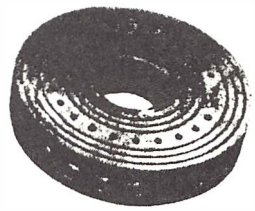


Figure 9.2.2

Lapped seal used in slide valve: (a) side view of Slide Valve; (b) cross section through the Slide Valve of an Exhaust Machine.

Figure 9.2.1

Each head is connected to the valve by an individual pipe (sweep). The heads are equipped with compression rubber fittings which provide an air-tight seal to the exhaust tube. A valve is integral with the exhaust head which either connects or isolates the lamp from the sweep to the center rotary valve.

In traveling around the machine, each lamp is first connected to a preliminary vacuum souce (rough pump) which reduces the pressure for a leak check. This is followed by more pumping (fine pump) and then flushing. Figure 9.2.3 shows a sequential operation. Figure 9.2.3 is not necessarily typical because different size lamps and production speeds require different cycles.

Typical Rotary Combination Flush and "Hard Pumping" System

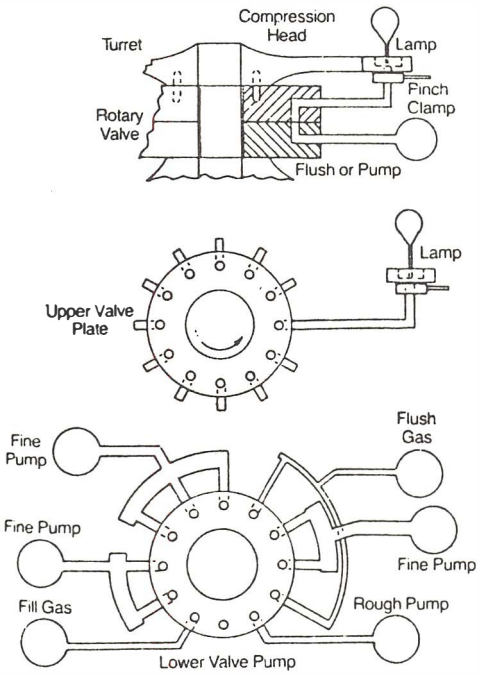


Figure 9.2.3

Rotary Fly Flush Pumping System

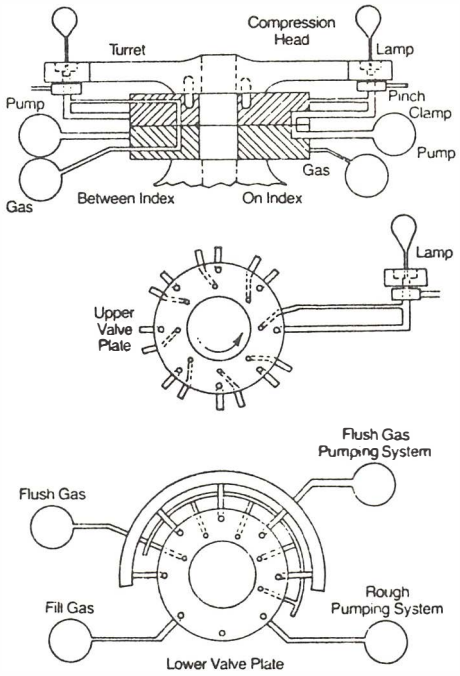


Figure 9.2.4

Figure 9.2.4 shows a system where less pumps and more flushing is utilized. The stationary rotary valve part (Figure 9.2.1 [b]) is the input for the vacuum pumps and the flush gas. The fill gas usually has a separate rotary valve that does not contain oil and sometimes the fill gas tank is mounted on the turret.

When the lamp has been pumped and flushed to the desired dilution level, the next step is to pump to as high a vacuum as practical within the time and equipment available. The next step is to fill the lamp to the required pressure. If there is any residual gas in lamp-head-sweep system before fill, the fill gas will push the gas into the lamp and thus change the gas mixture. In most cases this will not be terribly significant if residual gas is pure N_2. However, if the bulb is very small compared to the sweep, etc. the problem can be solved by pumping to a very low pressure before fill. After filling, the lamp is removed from the system by tipping-sealing off exhaust tube with a gas-oxygen flame.

There are a lot of variations in exhaust cycles, some machines employ fly flushing. In this operation, the flush gas port in the valve is half way between dwell positions. The gas is supplied to the lamp as the head port passes over the fly flush port during index. The time is so short, that only low gas pressure occurs - usually less than 100 Torr. When fly flush is used, as many as 9 flush-pump cycles are used. As speeds increase, fly flush becomes less attractive.

Filling is the opposite of pumping. When the bulb is at vacuum, the fill gas rushes into the lamp. As the pressure in the lamp increases, the pressure differential becomes less and the pressure rise rate decreases. For some lamps, more than one fill position is required. The fill gas pressure has a direct bearing on the performance of the lamp when it is put into service.

The final pressure in the lamp is a function of tipping technique.

9.3 TIPPING (PINCH OFF)

9.3.1 Vacuum Tip

This method requires that the pressure in the lamp be less than atmospheric. When heated, the exhaust tube collapses from external pressure and seals off the lamp. The tubing is then pulled to a thin thread of glass and severed by the flame. Excess glass is balled up on the tip by tipping fires and surface tension of the glass.

9.3.2 Press Tip

The press tip is accomplished by mechanically pressing the exhaust tube, after the tube is softened by heating. The process is critical because the pressure in the lamp is usually above atmospheric and will thus tend to expand and blow out when the glass is softened. Control is obtained by heating the shortest lengh of the tube necessary and to use a small bore heavy wall exhaust tube. Since a small bore is disadvantageous in pumping the tube is restricted by stretching just before the positive pressure is added. In this manner, a small bore, short section is achieved for pressing. Internal pressures up to 1200 Torr or more are possible with press tipping.

9.3.3 Freeze Out Tipping

In this method, the fill gas in the lamp is frozen by immersion of the lamp in liquid nitrogen. When the fill gas condenses, a vacuum results and the tip is a typical vacuum tip. After tipping, the fill gas vaporizes and final pressure is achieved. Fill pressure of 10 atmospheres or more are achievable by this method. (See Section 19.2.1 for addition details.)

FILL GAS

REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

1. Incandescent Lamps by W. G. Matheson, GTE Sylvania, Danvers, Massachusetts 01915.

2. Scientific Foundation of Vacuum Technique by S. Dushman, John Wiley & Sons, Inc., New York.

3. Exhaust & Fill Cycles for Incandescent Lamps by D. R. Dayton, GTE Sylvania, Danvers, Massachusetts.

4. Materials of High Vacuum Technology by Espe, Pergamon Press, 44-01 21st Street, Long Island City, New York 11101.

5. Gas Manufacturers Bulletins, Linde, Airco, Matheson.

6. Vacuum Sealing Techniques by A. Roth, Pergamon Press, 44-01 21st Street, Long Island City, New York 11101.

7. Exhaust Systems Training Package, GTE Sylvania Equipment Development Plant, Ipswich, Massachusetts.

8. Theory-Design and Installation of Rotary Exhaust Slide Valves by D. R. Dayton, GTE Sylvania, Estes Street, Ipswich, Massachusetts 01938.

9. The Collected Works of Irving Languir, Pergamon Press, 122 East 55th Street, New York, 22, New York, Volume II.

10.0 SELECTION OF HALOGEN DOSE COMPOSITION

There is no universal halogen dose, either in composition or percent of fill gas. Different types of lamps -- long life, short life, bulb size, bulb shape, quartz, vycor, hard glass, filament configuration, fill pressure, lamp burning position, lamp burning cycle, etc., all have an effect on the halogen cycle.

It is established that iodine is most suited for very long life lamps especially those of low wattage and current. A short life, high wattage lamp in small bulb might benefit from chlorine. Fluorine would probably be even better if the side effects can be neutralized.

There are many halogen doses in use. The composition of the dose does not change the fundamental chemistry of the tungsten transfer reactions.

IODINE

$$W + 2I \xrightarrow{>250^\circ C} WI_2$$

$$WI_2 \xrightarrow{>1200^\circ C} W + 2I$$

BROMINE

$$W + 3\,Br_2 \xrightarrow{>120^\circ C} WBr_6$$

$$WBr_6 \xrightarrow{>1100^\circ C} W + 6Br$$

CHLORINE

$$W + Cl_2 \xrightarrow{100^\circ C} WCl_6$$

$$WCl_6 \xrightarrow{>1700^\circ C} W + 6Cl$$

FLUORINE

$$W + 6F \xrightarrow{0^\circ C} WF_6$$

$$WF_6 \xrightarrow{>2700^\circ C} W + 6F$$

NOTE: All of the tungsten-halogen reactions require a small amount of oxygen for efficient transfer reactions. Carbon monoxide is considered to be the donor of the necessary oxygen.

Lamp Parameter Considerations when Selecting the Halogen Dose.

Wall loading and lamp life are variables which influence the selection of the Halogen dose. The following table shows some present trends.

Wall loading (Wcm^{-2})	Life (H)	Type of Halogen
60-100	0-100	HBr
30-60	0-500	HBr
15-30	500-1000	CH_2Br_2
15-25	500-2000	CH_3Br
15-25	> 2000	$CH_2Br_2 + I_2$
15-25	> 2000	CHI_3
15-25	> 2000	$CH_3I + CO + I_2$
15-25	> 2000	I_2
15-25	> 2000	$I_2 + CO$

10.1 Iodine I_2

Tungsten Transfer Reaction $W + 2I \quad WI_2$

$WI_2 \quad W + 2I$

Material: Analytical Reagent Trade Iodine Crystals

Iodine crystals are grayish-black

Iodine gas is blue-violet.

In a halogen lamp, the blue-violet gas absorbes 5 - 7% of the lumens. The lower the partial pressure of iodine gas, the more pale the color and the lower the loss in lumens.

VAPOR PRESSURE OF IODINE

°C	Torr
38.7	1
73.2	10
97.5	40
116.5	100
159.8	400
183.0	760

10.1.1 Iodine Dosing Procedure

There are two acceptable dosing procedures. For short run or experimental lamps, the following procedure can be used.

1. Pretolley lamp to clean up coil and bulb.
   This process includes pumping and flushing with forming gas or dry nitrogen, raising coil up to rated voltage, heating the quartz bulb and allowing the lamp to cool to room temperature before removing from compression head.

2. Put lamp in dry box
   Remove a small amount of iodine from container and put in exhaust tube about 10 mm back from open end of exhaust tube. Heat iodine deposit gently to fuse. No loose particles are permitted. Put cap on exhaust tube to protect iodine from atmosphere and remove lamp from dry box.

3. Remove exhaust tube cap and insert exhaust tube in exhaust trolley compression head. Cool iodine deposit area. A clamp which has been previously cooled by LN_2 or refrigeration and then clamped to exhaust tube is sufficient.
   Pump and flush the lamp a few times to insure a clean fill.
   The fill gas should contain about 0.03% oxygen.
   Fill lamp and tip as long as possible.
   Heat lamp with exhaust tube down and cooled with LN_2. This will recondense all iodine in the exhaust tube.
   Emerge lamp in a heated oil bath. (Oil bath temperature approximately 110°C) for about 1 hour or until the desired iodine color in lamp is observed. The iodine color will become more red with time.
   Remove lamp and wash oil off with hot water and immediately emerge one end of lamp in LN_2. The vaporized iodine will condense at the cool end. Now tip the lamp short to eliminate any iodine left in the exhaust tube. The lamp is now complete.

Production Method

1. Pretrolley lamp as in previous method.
2. Load lamp to compression head on rotary exhaust machine. The rotary exhaust is generally conventional with a castor oil sealed rotary plate valve, etc. Each head has an iodine pot. The iodine pot is a stainless steel vessel which is heated to about 45°C by resistance heaters. The vessel has a removable top and an outlet from inner chamber to a valve. Iodine is placed in the chamber and heated to generate an iodine vapor pressure in the chamber when the valve is closed. The iodine vapor pressure in pot will be approximately 3 Torr.
3. The general cycle is to pump and flush several times, pump to less than 1 Torr, cool a spot on lamp bulb by use of a liquid nitrogen jet, open valve on iodine pot for a controlled time. The iodine which has escaped from the pot will condense at cold spot. A black spot should be observed. After the iodine is deposited, the fill gas is added and the lamp tipped off. The lamp is now complete. If the fill was argon, liquid N_2 is used to condense the argon to obtain a vacuum for tipping and result in a pressurized lamp at room temperature.

It is necessary to have cold trap in sweeps to collect any iodine which might otherwise collect in rotary valve.

10.1.2 Equipment Contruction Materials

Stainless Steel, Monel and Viton or Teflon are acceptable construction materials.

10.1.3 Iodine Halogen Lamp Data

Long life halogen lamps are still mostly iodine. Elemental iodine is the most widely used dosing material for tungsten-iodine lamps of all types.

10.2 HYDROGEN IODIDE

(Synonym: Hydriodic Acid, Anhydrous)

(Formula: HI)

Description

Hydrogen iodide is a colorless, pungent, corrosive gas. It is over four times as heavy as air and fumes in moist air. It is supplied as a liquefied gas in cylinders at a pressure of about 95 p.s.i.g. at 70°F. Hydrogen iodide in the presence of heat or light will slowly decompose into hydrogen and iodine. For maximum stability, cylinders of hydrogen iodide should be stored at temperatures less than 34°F.

Toxicity

Hydrogen Iodide is a toxic gas. It is severely irritating to the upper respiratory tract and corrosive to the eyes.

Chemical Properties

Hydrogen iodide is exceedingly soluble in water; at 10°C. 100 g. water will absorb 234 g. hydrogen iodide, or 425 volumes hydrogen iodide per one volume of water. Hydrogen iodide is decomposed by light. It is the least stable of the hydrogen halides. Even at room temperature it dissociates slightly into its constituents.

TUNGSTEN TRANSFER REACTION

$$2\,HI \longrightarrow 2H + 2I$$

$$W + 2H + 2I \longrightarrow WI_2 + 2H$$

$$WI_2 \longrightarrow W + I_2$$

HYDROGEN IODIDE

Vapor Pressure vs Temperature

T°C	Torr	PSIA
0	2794	55
25	6096	120

10.2.1 Hydrogen Iodide Dosing Procedure

HI is mixed with the fill gas.

The procedure for preparing a tank of halogen dosed gas is outlined in Section 11.0.

10.2.2 Equipment Construction Materials

Anhydrous hydrogen iodide is essentially inert to metals and does not attack the commonly used structural metals (stainless steel, mild steel) under normal conditions of use (room temperature and atmospheric pressure). In the presence of moisture, however, hydrogen iodide will corrode most metals other than silver, platinum, and tantalum; carbon, graphite and impregnated carbon and graphite are recommended materials of construction for wet or dry hydrogen iodide. When used at higher pressures, it is necessary to use extra heavy black iron pipe throughout. No galvenized pipe or brass or bronze fittings should be used as these will corrode. High pressure steel, monel, or aluminum-iron-bronze valve should be used throughout. Users of hydrogen iodide are warned to always shut off their hydrogen iodide lines from the use end backward to the cylinders.

10.2.3 Hydrogen Iodide Lamp Data

HI is not generally used to dose halogen lamps because of the instability which results in lack of control of both the fill gas and lamp dose. Lamps made with HI lose the hydrogen by permeation through the quartz.

10.3 Methyl Iodide Chem. Formula CH_3I

TUNGSTEN	TRANSFER	REACTION
CH_3I	$\longrightarrow$	$C + 3H + I$
$2C + 6H + 2I$	$\longrightarrow$	$2C + WI_2 + 6H$
WI_2	$\longrightarrow$	$W + I_2$

The carbon can combine with the tungsten to form WC, or carbon can combine with any oxygen available to form CO and CO_2, any carbon which does not react condenses on the bulb wall resulting in a loss of lumens.

The deposition of carbon on bulb wall cannot be prevented, but by various control of lamp position and light up the carbon can be located in the least sensitive area, usually in the base area of the lamp.

The hydrogen will be lost early in life by permeation through the quarts bulb walls.

VAPOR PRESSURE OF METHYL IODIDE

$$\text{Log}_{10}\rho = \left(-0.2185 \times \frac{6616.5}{T°K}\right) + 7.403$$

Temperature	Pressure
0°C	Torr
0	128
25	356

10.3.1 Methyl Iodide Dosing Procedure

The CH_3I is mixed with the fill gas. A typical dose would be:

Krypton	98.95%
Oxygen	0.05%
CH_3I	1.00%

The procedure for preparing tank of halogen dosed fill gas is outlined in Section

10.3.2 Halogen Lamp Data

CH_3I has been used successfully to make long life halogen lamps.

Construction Material Data

No data available at this time.

10.4 Ethyl Iodide Chem. Formula C_2H_5I

TUNGSTEN TRANSFER REACTION

$$C_2H_5I \longrightarrow 2C + 5H + I$$

$$W + 4C + 10H + 2I \longrightarrow WI_2 + 4C + 10H$$

$$WI_2 \longrightarrow W + I_2$$

The carbon can react with the tungsten as any oxygen available as in CH_3I. The remaining carbon will deposit on the bulb wall and result in a loss of lumens. The more carbon atoms per needed iodine atoms, the more the problem with lumen loss. With C_2H_5I, there will be twice as many carbon atoms in the lamp for the same iodine dose. The hydrogen is not a problem as it will be lost early in lamp life by permeation through the quartz bulb walls.

VAPOR PRESSURE OF ETHYL IODIDE

$$\text{Log}_{10}p = \left(-0.2185 \times \frac{7851.8}{T°K}\right) + 7.88$$

Temperature °C	Pressure Torr
0	39.4
25	141.0

10.4.1 Ethyl Iodide Dosing Procedure

Same as CH_3I (Methyl Iodide)

10.4.2 Ethyl Iodide Lamp Data

Osram in Europe has used C_2H_5I with the same refrigeration fill system as for CH_2Br_2. No actual lamp data is available. Considerable lumen loss due to carbon deposited on bulb walls would be expected.

Construction Material Data

No Data is available. C_2H_5I is believed to be fairly inert.

10.5 Bromine Chemical Formula Br

Bromine is the only liquid nonmetallic element. It is a heavy, mobile, reddish-brown liquid, volatilizing readily at room temperature to a red vapor with a strong disagreeable odor, resembling chlorine, and having a very irritating effect on the eyes and throat; it is readily soluble in water or carbon disulfide, forming a red solution; it is less active than chlorine but more so than iodine; it unites readily with many elements.

TUNGSTEN TRANSPORT REACTION

$$W + 6Br \longrightarrow WBr_6$$

$$WBr_6 \longrightarrow W + 6Br$$

VAPOR PRESSURE OF BROMINE

Temp	Pressure
T°C	Torr
-48.7	1
-25.0	10
- 8.0	40
9.3	100
41.0	400
58.2	760

10.5.1 Bromine Dosing Procedure

Experimental lamps can be made by freezing out liquid Br in a Ta container, pump over the solidified Br to remove any air, O_2, N_2, etc. By use of a mamonneter, allow a measured pressure of Br to fill an evacuated clean lamp. Shut off source of Br and condense Br in lamp by liquid nitrogen jet or immerge part of lamp in liquid nitrogen. Add fill gas to desired pressure and tip off lamp.

10.5.2 Halogen Lamp Data

Too little Br results in lamp blackening. Too much Br causes attack of supports, coil ends and lamp leads. See Section 13.0 Lamp Construction materials for special data on low temperature W - Br- Pt reaction.

Bromine lamps have 5 - 7% higher efficiency than iodine lamps due to the difference in light absorption between iodine and bromine.

Results to date indicate that there is no chance of making lamps on a production basis with pure Bromine.

10.5.3 Equipment Construction Materials

Almost all materials are attacked by bromine.

Monel, Tantalum, Viton, Teflon and 316 stainless steel are considered acceptable for equipment construction materials.

10.6 HYDROGEN BROMIDE

(Synonym: Anhydrous Hydrobomic Acid) (Formula: HBr)

Description

Hydrogen bromide is a colorless, very irritating, corrosive gas at atmospheric temperature and pressure; as a liquid it has a yellow color. It is much heavier than air, and fumes in moist air. In cylinders, hydrogen bromide is a liquefied gas under its own vapor pressure of about 320 p.s.i.g. at 70°F. It is very souluble in water.

Toxicity

Hydrogen bromide is a toxic gas. It is severely irritating to the upper respiratory tract and corrosive to the eyes, skin and mucous membranes.

Chemical Properties

Hydrogen bromide is extremely soluble in water, forming a strong acid, and quite soluble in nonpolar solvents such as benzene. It is resistant to oxidation.

TUNGSTEN TRANSFER REACTIONS

$6HBr \longrightarrow 6H + 6Br$

$W + 6H + 6Br \longrightarrow WBr_6 + 6H$

$6H + WBr_6 \longrightarrow W + 6Br + 6H$ High temp. near Filament

$6Br + 6H \longrightarrow 6HBr$ Low temp. near bulb

HYDROGEN BROMIDE
VAPOR PRESSURE

°C	Torr	P.S.I.A
0	9144	180
25	17300	340

10.6.1 Hydrogen Bromide Dosing Procedure

HBr is mixed with the fill gas. The procedure for preparing a tank of HBr dosed gas is outlined in Section 11.0.

10.6.2 Equipment Construction Materials

Hydrogen bromide is essentially inert to metals and does not attack the commonly used constructural metals under normal conditions of use (room temperature and atmospheric pressure). In the presence of moisture, however, hydrogen bromide will corrode most metals other than silver, platinum and tantalum. When used at higher pressures, it is necessary to use extra heavy black iron pipe throughout. No galvenized pipe or brass or bronze fittings should be used as these will corrode. High pressure steel, monel or aluminum-iron-bronze valves should be used throughout. Users of hydrogen bromide are warned to always shut off their hydrogen bromide lines from the use end, backward to the cylinders.

HBr is absorbed on surface of most metals. It is usually necessary to passivate a system with HBr in order to control the amount of HBr arriving in a lamp compared to the amount of HBr entering the system. If the equipment is allowed to pump for a period of time, the HBr will be "pumped" off and a repassivation will be necessary. The standing time need only be an hour or so before HBr control is lost.

HBr is very detrimental to common mechanical vacuum pump oils. The oil looses its lubricating properties and the pump will seize. Some synthetic oils like ULVAC may be superior to mineral oils for pumps which see HBr. In any case, the pump parts should be stainless and viton where possible.

10.6.3 Hydrogen Bromide Lamp and Cycle Data

Hydrogen in addition to the bromine makes a significant difference in a tungsten bromine lamp. The HBr decomposes to H + Br at approximately 1600°C. Between 1600°C and 300°C atomic hydrogen and atomic bromine combine to form HBr. The result is that there is atomic Br in vicinity of hot filament to combine with the tungsten

form WBr_6 and near the bulb wall most of the Br has reacted with hydrogen to form HBr. HBr is reasonably inert to tungsten and, therefore, the cool supports and leads are not attacked as in pure bromine lamps. The affinity of Br for H is proved by the fact that the hydrogen does not permeate out of the lamp as in the case of HI lamps. Hydrogen is needed in a ratio of at least 1:1 for the Br. On long life Br lamps, the ratio may fall below 1:1 and lead attack will follow. The Platinum that is used as a weld flux for mounts accelerates the attack of Br on tungsten by a factor of 10. See Section 12.3 Construction of a Halogen Lamp for more detail.

Since the actual halogen cycle is still a Bromine cycle, a small amount of oxygen is needed in the form of CO to control rate of cycle.

The HBr lamp is severly affected by excess oxygen or small amounts of water vapor. A water cycle operates independent of the bromine cycle in removing tungsten from the filament. The bromine cycle has to work harder to keep the bulb walls clean. The effect can be seen in the first or second filament turns near the clamps.

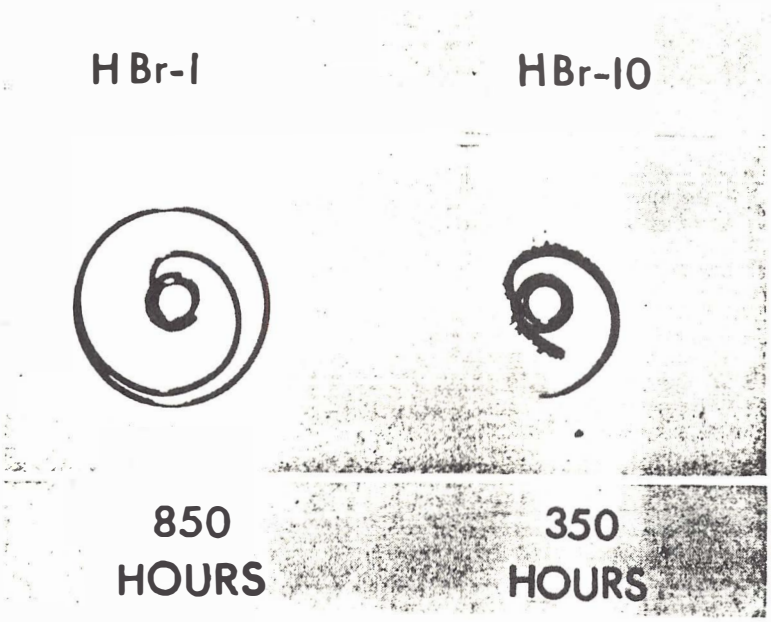
Too much HBr results in clean lamps and short life with attack on cool parts of coil, leads and supports. Too little HBr results in black lamps or black patches on bulb.

10.7 METHYL BROMIDE

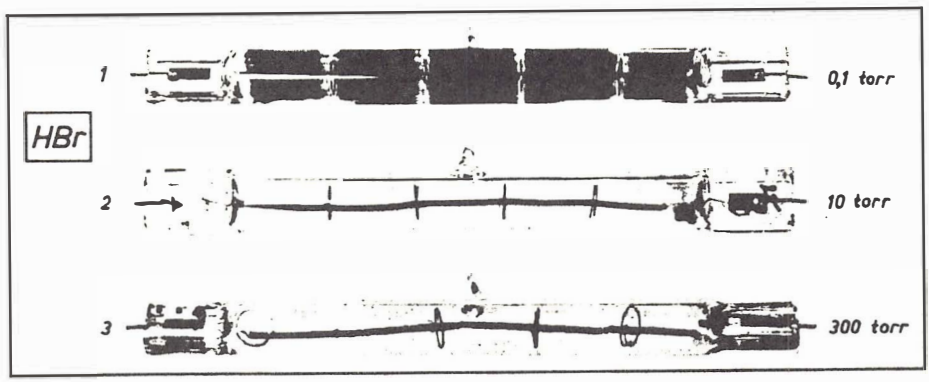
(Synonym: Bromemethane) (Formula: CH_3Br)

Description

Methyl Bromide is a colorless, poisonous gas at room termperature and pressure. It is easily liquefied and is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 13 p.s.i.g. at 70°F. It is odorless except in relatively high concentrations where it has a chloroform-like odor. It is practically nonflammable except in the narrow range 13.5-14.5% by volume in air. It is practically insoluble in water but soluble in the common organic solvents.



Comparison of attack on lamp supports operated in one and ten torr HBr.



Experimental lamps containing various amounts of HBr.
Lamp 1: after 17 hours the lamp is intact but blackened.
Lamp 2: failure after 28 hours.
Lamp 3: failure after 17 hours.

Toxicity

Methyl bromide is a highly toxic substance of insidious action. The odor of methyl bromide is not unpleasant and, therefore, it does not give definite warning in dangerous concentrations. Fatal poisoning, resulting from acute exposures to 8,600-60,000 p.p.m. of methyl bromide, is usually caused by its irritant effect on the lungs. In chronic poisoning, death is usually due to injury to the central nervous system. The onset of symptoms following the inhalation of methyl bromide is usually delayed, from 2-48 hours.

Chemical Properties

CH_3Br_2 reacts with magnesium to form the Grignard re-agent. It reacts with sodium (Wurtz synthesis), with alkali alkoxides (Williamson synthesis), with ammonia, with alkali hydrosulfides, with metal cyanides, with salts of carboxylic acids, and with sodio derivatives of active methylene compounds and acetylene compounds.

TUNGSTEN TRANSFER REACTION

$$CH_3Br \longrightarrow C + 3H + Br$$

$$W + 6C + 18H + 6Br \longrightarrow WBr_6 + 18H + 6C$$

$$18H + 6C + WBr_6 \longrightarrow W + 6Br + 18H + 6C \quad \text{near filament}$$

$$6Br + 18H \longrightarrow 6HBr + 12H \quad \text{near bulb wall}$$

The carbon will react with the filament to form WC, with oxygen to form CO_2 and CO. Any free carbon remaining will deposit on the bulb wall and reduce the lumens. The hydrogen in excess of an equal number of Br atoms (in this case [12]) will escape from the lamp by permeation through the quartz bulb walls. The loss in bulb transmittance in critical areas can be diminished by special light up procedures and bulb burning positions. The actual tungsten transfer cycle is still a basic bromine cycle.

METHYL BROMIDE
VAPOR PRESSURE

Temp	Pressure	
°C	Torr	PSIA
0°	760	14.96
25°	1525	30

10.7.1 Methyl Bromide Dosing Procedure

Same as HBr.

10.7.2 Equipment Construction Materials

Methyl bromide is not particularly corrosive to most metals. It is non corrosive when dry. However, it attacks aluminum and aluminum alloys (which should not be used as materials of construction) with the formation of aluminum trimethyl, which is spontaneusly flammable.

10.7.3 Methyl Bromide Lamp and Cycle Data

The dose has an equal number of carbon and Br atoms which will lead to light loss and maybe brittle filament ends. There is not much data available on CH_3Br lamps, but a well made CH_3Br lamp would be expected to have longer life than a HBr lamp.

Variation in the dose will have same effect as variation in HBr except that the higher the dose the higher the carbon added and the more light loss.

10.8 DIBROMOMETHANE Chemical Formula CH_2Br_2

Synonym: Methylene Bromide or Charlie Brown

Description

A clear, colorless liquid which boils at 97°C; miscible with organic solvents, slightly soluble in water; used as a solvent and chemical intermediate.

TUNGSTEN TRANSFER REACTIONS

$3\ (CH_2Br_2) \xrightarrow{>1500°C} 3C + 6HBr$

$3C + 6HBr \longrightarrow 3C + 6H + 6Br$

$3C + W + 6H + 6Br \longrightarrow WBr_6 + 3C + 6H$

$WBr_6 + 3C + 6H \longrightarrow W + 6Br + 3C + 6H$ near filament

$6Br + 3C + 6H \longrightarrow 3C + 6HBr$ near bulb wall

The carbon will react with W to form WC, with oxygen to form CO_2 and CO. Any excess carbon or unreacted carbon will deposit on the bulb wall. The carbon on bulb wall will reduce light output from lamp. The more carbon the more light loss and tendency for birttle filaments.

There is only half as much carbon reaction from CH_2Br_2 as with CH_3Br.

DIBROMOMETHANE
VAPOR PRESSURE

$$\text{Log } 10 = \left(-0.2185 \times \frac{8722.8}{T°K}\right) + 8.028$$

Temperature °C	Pressure Torr
0	10.92
25	42.88

10.8.1 Methylene Bromide Dosing Procedure

CH_2Br_2 is mixed with the fill gas. There are two methods of preparing the mixed gas. The general method of preparing a mixed tank is discussed in Section 11.0. However, due to the low vapor pressure of CH_2Br_2 at room temperature (25°C) there are some special considerations.

For practical reasons, the partial pressure of CH_2Br_2 in the mixed gas storage tanks should be less than the vapor pressure at room temperature. The reason is that should a decrease in temperature occur, condensation of the CH_2Br_2 would result in an unfavorable variation in the composition of the gas mixture. For this reason, the storage cylinders are normally filled with CH_2Br_2 to a maximum partial pressure of about 28 Torr. In practice, tanks are usually filled to either 5 or 10 atmospheres and CH_2Br_2 dose is usually 0.1 to 0.4%. The following table shows the limiting partial pressure mixtures as a function of tank pressure.

TANK PRESSURE	CH_2Br_2 % 0.1	0.2	0.3	0.4	0.5
5A (3800 Torr)	3.8 Torr	7.6 Torr	11.4 Torr	15.2 Torr	19 Torr
10A (7600 Torr)	7.6 Torr	15.2 Torr	22.8 Torr	30.4 Torr	

The table shows that for mixtures above 0.3% CH_2B4_2, low pressure tanks are required. For small lamps and low speed equipment, this is not a problem. For larger lamps at higher speeds, the tanks would have to be changed frequently.

STRATIFICATION IN FILL TANK

Although we have never identified this problem with HBr, the possibility of its occurrence is greater with CH_2Br_2 since the molecular weight is more than twice that of HBr. Thorn Lighting, Ltd., has reported cases where they have found it necessary to warm the bottom of the tanks in order to increase the molecular activity of the gases inside.

The Winchester system (keeping the tanks well above room temperature) should prevent any stratification.

ALTERNATIVE GAS MIXING PROCEDURE

In general terms, the system is as follows

Bubble the inert fill gas (Krypton for example) through a container of liquid CH_2Br_2. The fill gas picks up a large aount of CH_2Br_2. The fill gas and CH_2Br_2 passed through a temperature controlled cold trap. The vapor pressure of the CH_2Br_2 drops and excess condenses out leaving a selected partial pressure mixed with the fill gas. The mixed gas is then piped to exhaust machine at desired pressure.

This procedure eliminates tanks and has the ability to change the CH_2Br_2 fill gas content at will by changing the cold trap termperature.

The design of the equipment and operation is discussed in detail in Section 11.0 Fill Gas Mixing and Preparation.

10.8.3 Methylene Bromide Lamp and Cycle Data

Tests have proved that CH_2Br_2 has some oxygen gettering ability in addition to providing the HBr necessary for the tungsten halogen cycle. However, the lpw of CH_2Br_2 lamps is always less than that of comparable HBr lamps due to the carbon deposited on the bulb wall. The loss in lpw varies from 1% to 7% depending on the dose concentration and method of light up. A very slow initial light up is helpful. The dose is decomposed slowly and the carbon is

absorbed by the filament to a greater extent. The process may require 10 minutes for the initial light up operation. It is also possible to decompose the hydrocarbon halide (CH_2Br_2) outside the lamp during the filling, for example, by heating the exhaust tube during filling. In this method, an accurate control of the flow rate of the filler gas and of the tempearture of the exhaust tube is required. About 80% of the carbon can be removed by this method. Another procedure is to freeze out both the halide dose and the inert gas by emerging the lamp in liquid nitrogen. With inert gas condensed, about 80% of rated volts is applied across the lamp terminals. The voltage is increased within 20 seconds to 110% of the rated voltage. Decomposition of the dose occurs at a partial vacuum and in some way which is not obvious eliminates the carbon deposit on the bulb wall which would normally occur. Possibly the oxygen is not condensed and the carbon sees more oxygen than usual before depositing on the bulb wall. Any carbon which combined with oxygen would remain gaseous in the form of CO_2 or CO.

The potential advantages of CH_2Br_2 are:

1. Gettering action of carbon in lamp
2. Reduced machine maintenance
3. More consistant halogen dosing.

The possible problems and/or limitations of CH_2Br_2 are:

1. Carbon embrittlement of filament
2. Bulb discoloration
3. Low vapor pressure
4. Stratification in fill tank.

10.8.4 Carbon Embrittlement of Filament

The reaction of carbon with the tungsten coil can cause the filament to become brittle, resulting in "cold break" during shipping or when the lamp is subjected to mechanical shock. This problem is particularly severe in higher wattage lamps when a high level of bromine is required. If bromine is introduced into the lamp in the form of CH_2Br_2, an unacceptable amount of carbon can be introduced.

As an example, Erlangen was forced to modify the fill gas from CH_2Br_2 to HBr on FCS lamps to eliminate coil breakage.

10.9 BROMOFORM Chemical Formula $CHBr_3$

Synonym: Tribromomethane

Description

A colorless liquid, slightly soluble in water: used commonly in the separation of minerals.

TUNGSTEN TRANSFER REACTION

$$2(CHBr_3) \longrightarrow 2C + 2H + 6Br$$

$$2C + 2H + 6Br + W \longrightarrow WBr_6 + 2H + 2C$$

$$WBr_6 + 2H + 2C \longrightarrow W + 6Br + 2H + 2C \quad \text{near filament}$$

$$6Br + 2H + 2C \longrightarrow 4Br + 2HBr + 2C \quad \text{near bulb}$$

Note that there is an excess of free bromine. The results are somewhat unpredictable because in a very clean lamp the free bromine would attack the leads, supports, etc. much like a lamp made with a pure bromine dose. On the other hand, a lamp with a small amount of water vapor would benefit.

$$2C + 4Br + 2H_2O \longrightarrow 4HBr + 2CO$$

In other words, the excess Br would getter the hydrogen from decomposed H_2O and the carbon would getter the oxygen. This would be very desirable in some lamps and could result in short life clean lamp failure in other lamps.

BROMOFORM

VAPOR PRESSURE

$$\text{Log } 10 = \left(-0.2185 \times \frac{9673.3}{T°K}\right) + 7.8753$$

Temperature °C	Pressure Torr
0	1.358
25	6.06

The low vapor pressure makes this material difficult to use. The following table shows the tank pressure allowable for various % partial pressures of $CHBr_3$ in inert fill gas.

% $CHBr_3$	Tank Pressure (Atmospheres)
0.1%	6.57
0.2%	3.29
0.3%	2.20
0.4%	1.65

The % $CHBr_3$ would be low because of the 3 atoms of Br for each $CHBr_3$ molecule.

10.9.1 Bromoform Dosing Procedure

$CHBr_3$ is mixed with the fill gas. The procedure for preparing a tank of $CHBr_3$ dosed fill gas is outlined in Section 11.0

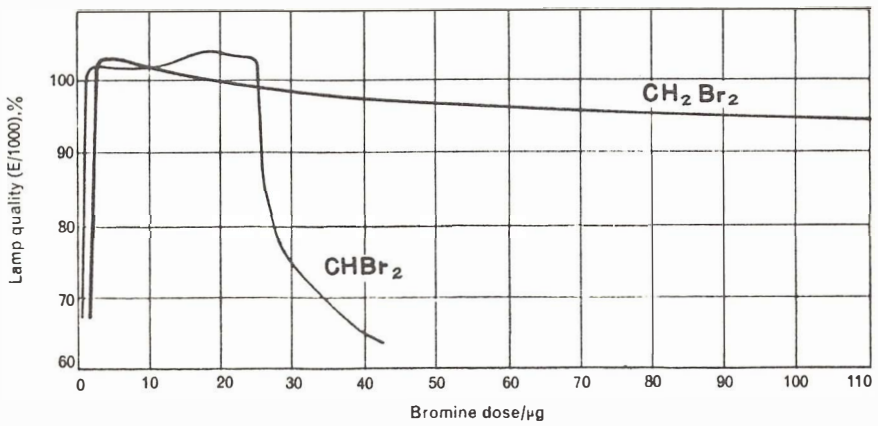
10.9.2 Equipment Construction Materials

There is little or no data available, but the same materials used for HBr would be suitable. That is stainless steel, Monel, Viton, Teflon, etc.

10.9.3 Bromoform Lamp and Cycle Data

There is not much data available, but this material should be useful in some lamp types. Especially highly loaded lamps in the medium life range 100 - 600 hours.

The following graph shows some life vs dose comparison for Bromoform ($CHBr_3$) and Dibromomethane (CH_2Br_2) dosed lamps.



The performance of 12 V 55 W tungsten-halogen lamps dosed with bromoform or dibromomethane

Figure 10.9.3.1

The shapes of the curves for bromoform and dibromomethane (Figure 10.9.3.1) are simlar at the low bromine doses but different for the higher concentrations.

The initial low-quality figures in both cases are due to insufficient bromine to react with the tungsten evaporating from the filament, resulting in bulb blackening and short useful lives. As the doses are increased the lamps remain clean for longer, until no bulb blackening is in evidence when the filament burns out. The minimum bromine doses required to prevent bulb blackening in this lamp are approximately 1.1 µg for bromoform and 2 µg for dibromomethane. This difference provides evidence that less free bromine is available for reaction with evaporated tungsten in the case of the additive dibromomethane than with bromoform.

On elimination of bulb blackening the quality of the bromoform-dosed lamps is then fairly constant until at approximately 25 µg bromine, when the lamp lives start to be reduced by tail attack. This takes the form of erosion of the filament tail where it enters the pinch seal, coupled with tungsten crystal growths just above this point on the tail. The point of attack of a filament tail will clearly be temperature dependent, and in this lamp appears to occur at the coolest point readily accessible to the halogen. Further increases in bromine concentration result in faster erosion of the tail and earlier lamp failures.

The shape of the curve above 2 µg is very different where dibromomethane is the additive. Even at lamp doses of 110 µg bromine no tail attack was observed with dibromomethane. Since over the whole concentration range the only major difference between the two compounds is their H/Br ratio, the effect of hydrogen in reducing tail attack is clearly demonstrated.

Although for the dibromomethane-dosed lamps there is no dramatic fall in lamp life as for bromoform, there is a gradual decrease in lamp quality. This effect is ascribable largely to the deposition of carbon on the bulbs, which was clearly visible in the high-dosed

lamps and which was also readily noticeable photometrically in the decreasing light output of the lamps with increasing dose. These results clearly demonstate the effect of compounds with insufficient hydrogen to satisfy the bromine, such as bromoform, are used in these lamps the dose must be accurately controlled to avoid bulb blackening at low doses and tail attack at high doses.

10.9.4. Effect of Added Water (See also Section 3.6.2.3)

Three types of filament failure were observed in this trial:

i. Normal failure: failure at a point near the center of the filament coil where it is hottest, probably due to normal evaporation of tungsten

ii. Tail failure: the high-dosed bromoform lamps, with little or no added water, failed as expected at the base of the tail where it enters the pinch seal. As already described, this is associated with attack by free bromine.

iii. Water failure: the effect of water was observed as thinning of the penultimate turn of the filament, accompanied by crystal growth on the end turn and upper region of the filament tail. Lamps affected failed either by melting of the thinning turn or when a crystal growth extended across between the first two turns.

The high-bromine/high-water-content lamps developed reddish-brown deposits in the cool pinch corners during life; these were assumed, although not proven, to be tungsten oxybromides. The high-water/low-bromine lamps showed whitish films on the bulbs early in life, probably a tungsten oxide.

The addition of water to tungsten-bromine lamps might be expected to result in a water-vapor cycle causing erosion of the filament and reduction of lamp life. The experimental results indicate that the concentration and composition of the organic bromide also present have a substantial effect on the activity of the water cycle.

Bromoform appears to have a particularly strong nullifying effect on the water cycle, a property which is ascribable to its lack of sufficient hydrogen to satisfy completely the bromine present.

10.10 MERCURIC BROMIDE Chemical Formula $HgBr_2$

$HgBr_2$ is non-volatile at room temperature.

TUNGSTEN TRANSPORT REACTION

$$6HgBr_2 \longrightarrow 3Hg_2Br_2 + 3Br_2$$

$$W + 3Hg_2Br_2 + 3Br_2 \longrightarrow WBr_6 + 3Hg_2Br$$

$$WBr_6 + 3Hg_2Br_2 \longrightarrow W + 6Br + 3Hg_2Br_2 \quad \text{near filament}$$

$$6Br \longrightarrow 3Br_2 \quad \text{near bulb wall}$$

This material will attack the supports, loads, etc. similar to a pure bromine lamp.

10.10.1 Mercuric Bromide Dosing Procedure

The dose is added directly to lamp. Fill gas is added later.

Since $HgBr_2$ is non-volatile at room temperature, it can be readily introduced into the lamp by various means. For example, a carefully weighed quantity of $HgBr_2$ can simply be dropped into the lamp envelope through the exhaust tubulation before the latter is tipped off and sealed. The required amount of $HgBr_2$ can also be pressed into pellets to facilitate dosing in this manner. The $HgBr_2$ can also be dissolved in a suitable volatile solvent, such as benzene, and a measured volume of the resulting solution dispensed into the envelope through the exhaust tube to provide a "liquid-dosing" method.

The dose is in the order of 0.22 - 0.43 micromole per milliter of bulb volume.

10.10.2 Halogen Lamp and Data Cycle

There is not data available except that written up in U.S. Patent #4,020,380 by Avinash D. Kulkarni assigned to Westinghouse.

10.10.3 Chlorine Chemical Formula Cl

There is no data regarding lamps dosed with pure chlorine. However, since chlorine is more active than bromine, all the problems encountered with pure bromine would be worse with chlorine.

10.11 HYDROGEN CHLORIDE

(Synonym: Anhydrous Hydrochloric Acid)

(Formula: HCl)

Description

Anhydrous HCl is a colorless, pungent corrosive gas having a suffocating odor. Hydrogen chloride is heavier than air and fumes strongly in moist air. It is very soluble in water and alcohol, and also soluble in ether.

Toxicity

Hydrogen chloride is a highly toxic gas; it is severely irritating to the upper respiratory tract and corrosive to the eyes, skin, and mucous membranes. The acid formed neutralizes the alkali of the tissues and causes death as a result of edema or spasm of the larynx and inflamation of the upper respiratory system. Hydrogen chloride provides adequate warning for prompt voluntary withdrawal from contaminated atmospheres.

Chemical Properties

Hydrogen chloride is thermally stable, being 0.22% dissociated into hydrogen and chlorine at 1810°K. Hydrogen chloride is stable to oxidation except at elevated temperatures. Hydrogen chloride is extremely soluble in water. Its aqueous solution is a strong acid.

TUNGSTEN TRANSFER REACTION

$$6\,HCl \xrightarrow{> 1810^\circ K} 6H + 6Cl$$

$$W + 6H + 6Cl \longrightarrow WCl_6 + 6H$$

$$6H + WCl_6 \longrightarrow W + 6Cl + 6H \quad \text{near filament}$$

$$6H + 6Cl \longrightarrow 6HCl \quad \text{near bulb wall}$$

HYDROGEN CHLORIDE

VAPOR PRESSURE

Temperature	Pressure	
°C	Torr	PSIA
0		350
25		650

10.11.1 HCl Dosing Procedure

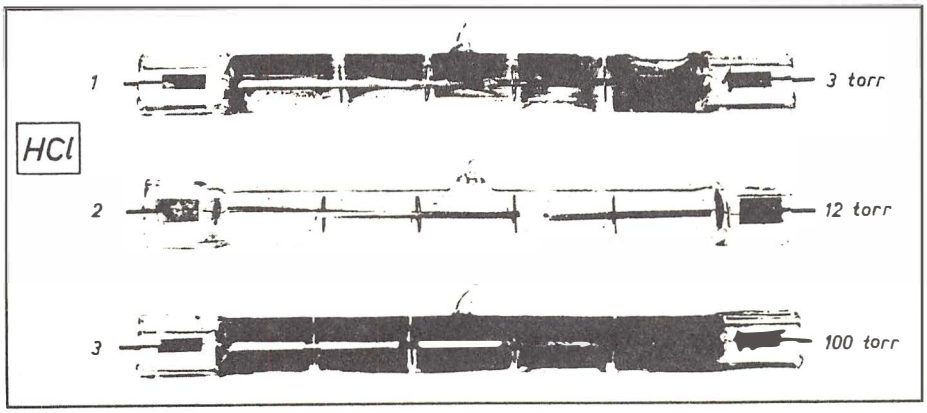
HCl is mixed with the fill gas. The procedure for preparing a tank of HCl dosed gas is outlined in Section 11.0.

10.11.2 Equipment Construction Materials

Hydrogen chloride is essentially inert to metals and does not attack the commonly used structural metals (stainless steel, mild steel) under normal conditions of use (room temperature and atmospheric pressure). In the presence of moisture, however, hydrogen chloride will corrode most metals other than silver, platinum, and tantalum, but moist or dry hydrogen chloride can be handled in baked carbon, graphite, and impregnated carbon and graphite materials. When used at higher pressures, it is necessary to use extra heavy black iron pipe throughout. No galvanized pipe or brass or bronze fittings should be used as these will corrode. High pressure monel or aluminum-iron-bronze valves should be used throughout. Users of hydrogen chloride are warned to always shut off their hydrogen chloride lines from the use end, backward to the cylinders.

10.11.3 Hydrogen Chloride Lamp and Cycle Data

There is not much test data available. However, it would be expected that lamps would remain clean with lower bulb wall temperatures than with HBr. The required dose would be less and more critical than for HBr.



Experimental lamps containing various amounts of HCl.
Lamp 1: after 15 hours the lamp is intact but blackened.
Lamp 2: failure after 33 hours.
Lamp 3: after 15 hours the lamp is intact but blackened.

Figure 10.11.3.1

At the same temperature, the stability of the tungsten-halide increases in the sequence iodine-bromine-chlorine. This means that in the cooler regions of the lamp the conversion of tungsten to halide takes place more easily, so that the danger of blackening in this sequence is reduced. In the hot parts of the lamp, however, the dissociation of the halide in this sequence is more difficult. In the immediate vicinity of the central part of the filament, however, the dissociation is still amply sufficient for all three halogens.

The problem with the chemical attack of the ends of the filament appears to be greatest with chlorine. For this halogen the equilibrium shifts fastest towards the halide when the temperature is lowered, and therefore the danger of the undesired attack of leads, supports, and filament tails is the greatest.

10.11.3.1 Long Life Lamp Problems

When the experiments with HCl and HBr were extended to types of lamps which were required to have lives of several thousands of hours, complications were encountered. While the lamp is operating, hydrogen escapes through the quartz wall, resulting in a continuous increase in the concentration of free halogen. The behavior of the lamp over a long period then corresponds in many ways to that of the lamp with a pure halogen filling over a shorter period, the result being serious attack of the ends of the filament and the filament supports.

NOTE: Chemical transport reactions in the tungsten-chlorine system are substantially influenced by hydrogen. A system consisting of a tungsten wire burning to incandescense in a quartz bulb in the presence of a chlorine-containing atmosphere has been shown to exhibit tungsten transport in the cold to hot direction, i.e., from the bulb to the wire. If hydrogen is added to this system, e.g., by hydrogen diffusion through the hot quartz bulb, and the hydrogen concentration exceeds a chlorine-to-hydrogen ratio of 1.4:1, the direction of tungsten support is changed to the hot to cold direction and the bulb begins to blacken.

See Figure 10.11.3.1 - Lamp 3

We have more to learn about this reversal in tungsten transport direction or the change in tungsten to tungsten halide conversion efficiency at the wall with higher HCl dosing.

10.12 TRICHLOROMETHANE OR CHLOROFORM Chemical Formula $CHCl_3$

Description

A colorless, sweet-smelling, nonflammable liquid, $CHCl_3$ has a boiling point of 61.2°C and a specific gravity of 1.489. The material has been used as an anesthetic. It decomposes easily in the presence of light to form phosgene.

Toxicity

Chloroform is toxic, and the fumes are injurious when breathed or absorbed through the skin.

TUNGSTEN TRANSFER REACTION

$$2CHCl_3 \longrightarrow 2C + 2HCl + 2Cl_2$$

$$W + 2C + 2HCl + 2Cl_2 \longrightarrow WCl_6 + 2H + 2C$$

$$WCl_6 + 2H + 2C \longrightarrow W + 2HCl + 2Cl_2 + 2C$$

The carbon would be converted to CO or CO_2. The net effect would be similar to a pure chlorine lamp. However, the affinity of chlorine to combine with hydrogen could result in gettering action in a lamp with a water cycle.

CHLOROFORM VAPOR PRESSURE

°C	Torr
-58	1
-29.7	10
- 7.1	40
+10.4	100
+42.7	400
+61.3	760

10.12.1 Chloroform Dosing Procedure

$CHCl_3$ vapor is mixed with the fill gas. The procedure for preparing a tank of $CHCl_3$ dosed gas is outlined in Section 11.0.

10.12.2 Equipment Construction Materials

Stainless Steel type 316 or 304 is recommended. Viton is recommended for rubber components.

10.12.3 Chloroform Lamp and Cycle Data

Experiments were carried out using a $CHCl_3$ containing lamp having a rated voltage of 100 V, a power of 300 W and a rated life duration of 500 hours. With a lamp of such type, it is easy to observe such phenomena as blackening and etching since the temperature of the filament is relatively high and the diameter of the filament is thin.

In the experiment, a plurality of lamps were prepared by selectively sealing therein, together with argon used as an inert gas, 0.005 micromol, 0.01 micromol, 0.05 micromol, 0.10 micromol, 0.15 micromol and 0.20 micromol of $CHCl_3$ per cubic centimeter of the inner volume thereof. The pressure of the gas charged in each of the lamps was maintained at 600 to 700 mm Hg. The lamps were operated at a rated voltage of 100 V and 10 percent overvoltage of 110 V. The results are shown in the table below.

(Table on following page)

Amount of sealed $CHCl_3$ (micromol/$cm.^3$)	Working Voltage (Volt)	Remarks
0.005	100	Blackening appeared 34 hours after ignition of the lamp.
0.005	110	Same as the above.
0.010	100	Blackening and etching did not appear 1650 hours after ignition though the filament was burned out.
0.010	110	Same as the above.
0.050	100	Blackening and etching did not appear 1433 hours after ignition of the lamp.
0.050	110	Same as the third and fourth columns.
0.100	100	Blackening and etching did not appear 1360 hours after ignition though the filament was burned out.
0.100	110	Blackening and etching did not appear 590 hours after ignition though the filament was burned out.
0.150	100	Etching appeared 500 hours after ignition.
0.200	100	Etching appeared 280 hours after ignition.

It will be apparent from the table that the amount of incorporation of $CHCl_3$ of 0.01 to 0.10 micromol/cm^3 causes the lamps to be maintained at high efficiency without the occurrence of blackening and etching during the operative life thereof.

The amount of incorporation of chloroform according to this invention is selected to lie within the range of 0.01 to 0.10 micromol/cm^3 on the basis of the results of the foregoing experiments. The selection of the amount of incorporation at that range is due to the fact that lamps of a predetermined life will not be definitely produced due to production errors when said amount is closely out of that range. The range described will definitely permit lamps of a predetermined life to be manufactured at allowances of usual production errors permissible in the art.

10.13 CARBON TETRACHLORIDE Chemical Formula CCl_4

(Synonym: Tetrachloro Methane)

Description

A heavy colorless liquid, one of a group of chlorinated hydrocarbons. It is widely used as a degreasing and cleaning agent in dry cleaning and textile industries. It is non-inflammable.

Toxicity

CCl_4 is quite safe at room temperature. It is used as a chemical in fire extinguishers, but when it falls on hot metal it dissociates and forms the poisonous gas known as phosgene.

TUNGSTEN TRANSFER REACTION

$$3CCl_4 \longrightarrow 3C + 6Cl_2$$

$$2W + 3C + 6Cl_2 \longrightarrow 2WCl_6 + 3C$$

$$2WCl_6 + 3C \longrightarrow 2W + 6Cl_2 + 3C$$

The carbon would be converted to CO or CO_2. The net result would be a lamp identical to a pure chlorine lamp. However, the affinity of chlorine to combine with hydrogen could result in gettering a lamp with a water cycle.

$$2CCl_4 \longrightarrow C + 2Cl_2 \longrightarrow C + 4Cl$$

$$2H_2O \longrightarrow 2O + 4H$$

$$4H + 4Cl + C + 2O \longrightarrow 4HCl + CO_2$$

With this added water, the lamp would function as a HCl lamp.

CARBON TETRACHLORIDE VAPOR PRESSURE

$$\text{Log}_{10} P = \left(-0.2185 \times \frac{8271.5}{^\circ K}\right) + 8.05$$

Temperature °C	Pressure Torr
0	26.9
25	96.6

10.13.1 Carbon Tetrachloride Dosing Procedure

CCl_4 vapor is mixed with the fill gas. The procedure for preparing a tank of CCl_4 dosed gas is outlined in Section 11.0

10.13.2 Equipment Contruction Materials

Standard Lamp Equipment Construction materials are satisfactory.

10.13.3 Carbon Tetrachloride Lamp and Cycle Data

Very little work has been done with CCl_4 dosed lamps. The available data indicate a very critical dose.

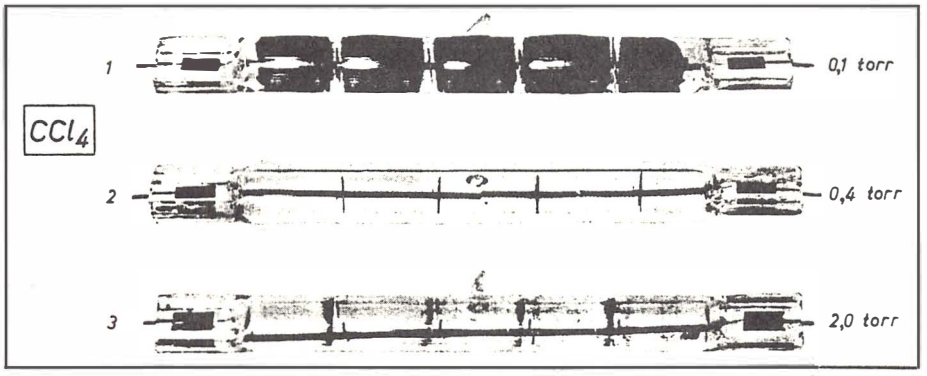


Figure 10.13.3.1

Experimental lamps (225 V, 1000 W, 12 cm length) containing various amounts of carbon tetrachloride.
Lamp 1: after operating for 5 hours the lamp is still intact but shows severe blackening.
Lamp 2: failure after 26 hours
Lamp 3: failure after 3 hours.

For chlorine at relatively low partial pressures, the cycle works quite well at the beginning of the operation: the bulb remains clear. After a certain operating time, however, fairly serious blackening suddenly appears. The life is normal, i.e., about 30 hours.

With relatively large quantitites of chlorine there is no blackening at all during the whole period of operation; the cycle is obviously working well. The life, however, is much shorter -- sometimes even as short as 10 minutes with chlorine. The filament shows strong local dendritic growth, and the supports have been attacked.

10.14 FLUORINE Chemical Formula F_2

Description

Fluorine is a highly toxic and corrosive pale yellow gas, with a sharp, penetrating, and characteristic odor. It is shipped in steel cylinders as a nonliquified gas.

Toxicity

Fluorine is a highly toxic gas. Fluorine has a sharp, penetrating and characteristic odor, detectable in very low concentrations. Because of this, the inhalation of seriously toxic quantities is unlikely. The inhalation of high concentrations of fluorine would cause asphyxia, and subsequently would result in severe lung congestion. A victim overcome by fluorine must be removed to an uncontaminated area and a physician should be called immediately.

Chemical Properties

Fluorine is the most powerful oxidizing agent known, reacting with practically all organic and inorganic substances with the exception of metal fluorides in their highest valence state and a few pure completely fluorinated organic compounds. Even the latter may burn in a fluorine atmosphere if contaminated with a combustible material or if subjected to high flow rates of fluorine. Hydrogen and fluorine combine with extreme violence forming hydrogen fluoride. Oxygen does not ordinarily react with fluorine but two oxygen fluorides, OF_2 and O_2F_2, are known. The halogens from compounds of the type ClF, ClF_3, BrF_3 and IF_5. Carbon, as such, or the majority of hydrocarbons, on reaction with excess fluorine form carbon tetrafluoride with small amounts of tetrafluorethylene or hexafluoropropene. Nitrogen is generally inert toward fluorine and may be used as a diluent for vapor-phase reactions. Fluorine will displace other halogens from many such halogen-containing compounds. The reaction of most organic compounds with fluorine will occur explosively.

Passivation Procedure

Prior to the placing of any equipment, lines or fittings in service, they must be thoroughly cleansed of all foreign matter, flushed

with a nonaqueous degreasing solvent such as acetone, trichloroethylene or carbon tetrachloride, then thoroughly purged with a stream of dry nitrogen. The equipment is then ready for passivating.

The passivating procedure consists of slowly displacing the dry nitrogen in the system by bleeding fluorine into the system (at essentially atmospheric pressure, and a nominal rate of 0.1 to 0.3 g/mole of fluorine per hour for laboratory sized systems). Continue the displacement procedure until a piece of filter paper or swatch of cotton held close to the exit by means of long metal forcepts, begins to burn. The system is then valved off and the working pressure of fluorine is applied, After five to ten minutes, passivation is assumed to be complete. The fluorine system is then flushed with dry nitrogen and sealed until put into service.

Passivation may also be achieved by use of chlorine trifluoride in the manner described for fluorine.

TUNGSTEN TRANSFER REACTION

Fluorine is the only element to react at room temperature with tungsten and carbon, giving the gaseous fluorides WF_6 and CF_6.

$$W + 3F_2 \longrightarrow WF_6$$

$$WF_6 \xrightarrow{>3000°K} W + 6F$$

The cycle can be maintained at any bulb temperature.

FLUORINE VAPOR PRESSURE

Fluorine has a vapor pressure of 1 atmosphere at minus 188°C.

10.14.1 Fluorine Dosing Procedure

Fluorine by itself is very difficult to handle. Therefore, it is preferable to use fluorine compounds for dosing.

10.14.2 Equipment Contruction Materials

The reaction of fluorine with many metals is slow at room temperature and often results in the formation of a metal fluoride film (see Passivation Procedure). This film retards further attack in the case of certain metals such as brass, iron, aluminum, magnesium and

copper and hence these metals are quite satisfactory for handling fluorine at room temperatures. Nickel and monel are by far the best materials to use at high temperatures.

10.14.3 Fluorine Lamp and Cycle Data

No data is available on lamps made with pure fluorine. It would be expected that the quartz would be attacked at 100°C or more and cycle would get out of control.

Tungsten hexafluoride is the most favored species at lower temperatures and the reaction occurs as:

$$SiO_2 + WF_6 \longrightarrow SiF_4 + WO_2F_2$$

The oxyfluorides subsequently dissociate to tungsten oxides, which deposit on the lamp envelope.

$$2WO_2F_2 \longrightarrow WOF_4 + WO_3$$

The formation of silicon tetrafluoride, SiF_4, means that fluorine is "trapped," i.e., free fluorine atoms cannot form at the filament temperature and therefore cannot participate in a transport cycle. Consequently the formation of tungsten oxide on the envelope is followed by the deposition of a thick opaque tungsten film rendering the lamp useless after only a few minutes operation.

10.15 BROMOTRIFLUOROMETHANE Chemical Formula $CBrF_3$

(Synonym: Freon-13B1)

Description

Bromotrifluoromethane is a colorless, non-inflammable, noncorrosive gas. It is shipped as a liquefied gas under its own vapor pressure of about 190 p.s.i.g. at 70°F.

Toxicity

Bromotrifluoromethane is comparatively non-toxic. Concentrations up to at least 20% by volume in air do not produce any perceptible injury on exposures of 2 hours. However, bromotrifluoromethane is not entirely without physiological effect, particularly in acute exposures.

Chemical Properties

Bromotrifluoromethane is thermally stable. Anhydrous $CBrF_3$ or $CBrF_3$ with 3% (by volume) of water is not corrosive to steel, brass, or aluminum after exposure at 248°F (120°C) for 260 days. Copper and stainless steel show no detectable corrosion upon immersion for 7 days in bromotrifluoromethane containing 3 volume % water.

TUNGSTEN TRANSFER REACTION

$$CBrF_3 \xrightarrow{>800°K} C + Br + 3F$$

$$W + 3C + 3Br + 6F \longrightarrow WF_6 + 3Br + 3C$$

The Br is available as a hydrogen getter and the carbon is available as an oxygen getter.

$$WF_6 \xrightarrow{>3000°K} W + F_6$$

At this point, the cycle would be the same as a pure F_2 cycle. However, it has been found that the oxygen balance is critical and if there is an oxygen atom for each fluorine atom the compound WOF_4 will be formed. The presence of a little oxygen prevents attack of the quartz and cooler parts of mount.

10.15.1 $CBrF_5$ Dosing Procedure

$CBrF_5$ vapor is mixed with the fill gas. The procedure for preparing a tank of $CBrF_5$ dosed gas is outlined in Section 11.0.

10.15.2 Equipment Construction Materials

Most of the commonly used metals (steel, brass, aluminum, copper, stainless steel) may be used satisfactorily with bromotrifluoromethane numder normal conditions of use.

Washers made from Kel-F or from vulcanized fiber showed no swelling or other adverse effects when immersed in liquid bromotrifluoromethane for 2 weeks.

Piping and vessels to contain bromotrifluoromethane should be adequately designed to withstand the pressures to be encountered.

10.15.3 $CBrF_5$ Lamp and Cycle Data

The use of fluorine-containing compounds in tungsten halogen lamps has been reported with claims of substantial improvements over tungsten bromine lamps. Fluorine was added as gaseous $CBrF_3$ which on decomposition would produce BrF_3 as the active fluorinating agent. This compound is stable to 2000°K which accounts for the limited attack on the bulb wall and filament tails reported. Tail erosion at higher oxygen partial pressures is consistent with the increased rate of reactivity resulting from the formation of excess tungsten oxybromides and oxyfluorides.

The fill gas was Kr (99.995% purity) with varying concentrations of $CBrF_3$.

There was no observable attack throughout the operating life of either the lamp walls or the filament legs near the walls for $CBrF_3$ concentrations up to 500 ppm. Therefore, there appeared to be no fluorine (or HF) in the cooler regions.

Life was measured by operating the lamps at 14.00 ± 0.05 V dc, which produced a filament temperature of 3250°K. for a group of lamps with a fixed $CBrF_3$ concentration was determined by plotting time-to-failure on a Weibull plot.

An example is shown in Figure 4 where the distribution has been approximated by a straight line. The intersection of the 50% failure point with this line is taken as the rated life. For the group of lamps in Figure 4, the fill gas contained 100 ppm of $CBrF_3$, and the life was 355 h. Life figures for other concentrations of $CBrF_3$ are listed in Table 1. Note that higher and lower concentrations yield significantly lower life, indicating that the required fluorine-oxygen balance for lamps fabricated as described above occurs at $CBrF_3$ concentrations of $\sim$ 100 ppm.

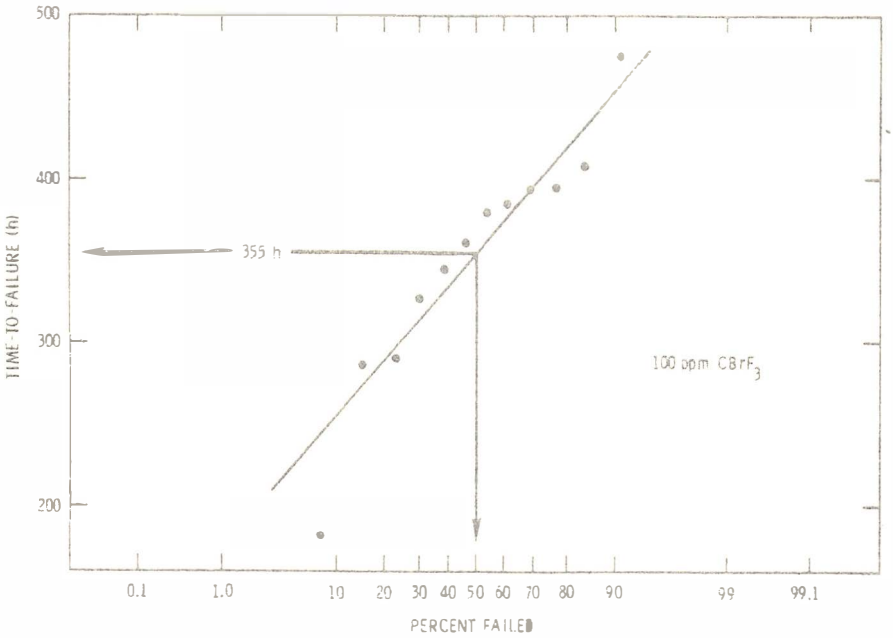


Figure 4

Weibull plot of time-to failure versus percent failed for lamps with 100 ppm of $CBrF_3$

TABLE I

Average Life at Different $CBrF_3$ Concentrations

$CBrF_3$ Concentration (ppm)	Life (h)
50	250
100	355
250	205
0 $CBrF_3$ replaced by CH_2Br_2	140

In order to confirm that the use of fluorine actually extends life a control group of lamps was fabricated in the same manner except that $CBrF_3$ was replaced by 500 ppm of methylene bromide (CH_2Br_2). This concentration of CH_2Br_2 was previously determined to be optimum for lamps fabricated with more normal extensive processing.

However, as shown in Table 1 , for lamps without extensive processing the life is reduced to about 40% of that for fluorine-containing lamps. Therefore, we conclude that a fluorine cycle can more than double lamp life.

The results of deviating from the necessary fluorine-oxygen balance were confirmed by examination of lamps after failure. Figure 5 (a) is a photomicrograph of a lamp for which F:O > 1:1. Note that both deposition of tungsten and leg erosion have occurred as predicted. An example from a lamp with F:O $\cong$ 1:1 is shown in Figure 5 (b) where there is no evidence of either tungsten decomposition or leg erosion. The concentrations of $CBrF_3$ at which life is a maximum and F:O-1:1 agree within a factor of 2; therefore, both the fluorine and the oxygen content must be controlled to realize a practical fluorine cycle.

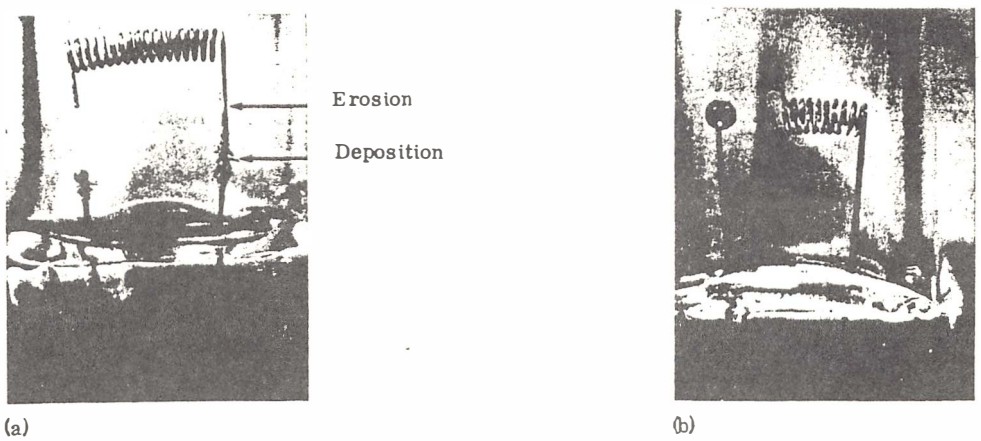


Figure 5

Photomicrographs of lamps after failure with (a) F:O > 1:1 and (b) F:O $\cong$ 1:1.

10.16 NITROGEN TRIFLUORIDE Chemical Formula: NF_3

Description

Nitrogen trifluoride is a colorless, stable toxic gas with a

characteristic moldy odor. It is supplied in steel cylinders as a nonliquefied gas at 200 p.s.i.g. at 70°F (cylinder pressure). It is somewhat soluble in water without reaction and is not affected by dilute basic or acid solutions at low temperatures.

Toxicity

Nitrogen trifluoride is a toxic gas. The 1968 American Conference of Governmental Industrial Hygienists has recommended a threshold limit value of 10 ppm for nitrogen trifluoride (concentration in air to which nearly all workers may be exposed, day after day, without adverse affects). Inhalation of higher concentrations may cause irritation of the respiratory tract, headache, nausea, and diarrhea.

Chemical Properties

Nitrogen trifluoride is very stable. It does not react with water at 133°C. It is slowly hydrolyzed by dilute bases at 100°C. Nitrogen fluoride reacts with various metals, such as copper, bismuth, arsenic, antimony, stainless steel and mercury, at elevated temperatures (around 350°C) to form tetrafluorohydrazine. Nitrogen fluoride reacts with hexafluoropropylene over sodium fluoride at 520°C. to give mainly iso-C_3 to C_6-fluorocarbons and fluorocarbon imines. Nitrogen fluoride reacts with hexafluoropropylene over cesium fluoride at 320°C to give, as major products, $(CF_3)_2CFCF(CF_3)_2$, $(CF_3)_2CFNF_2$, and $(CF_3)_2C{:}NF$. Although nitrogen trifluoride is a strong oxidizing agent, it is surprisingly inert at ordinary temperatures.

TUNGSTEN TRANSFER REACTIONS

$$2NF_3 \longrightarrow 2N + 6F$$

$$W + 2N + 6F \longrightarrow WF_6 + N_2$$

$$WF_6 \xrightarrow{> 3000°K} W + 6F$$

Vapor Pressure

The vapor pressure of liquid nitrogen trifluoride up to boiling point is expressed by the following equation:

$$\text{Log}_{10}\rho = 6.77966 - \frac{501.913}{T-15.37} \qquad \begin{matrix}\rho = \text{mm. Hg} \\ T = °K\end{matrix}$$

The vapor pressure from the boiling point to the critical point is expressed by the following equation[1]:

$$\text{Log}_{10}\rho = 4.27264 - \frac{613.33}{T}$$

ρ = mm. Hg
T = °K

Temperature	Pressure	
0°C	Torr	PSIA
-129.0	760	14.96
25	50,800	1000

10.16.1 NF_3 Dosing Procedure

NF_3 is mixed with the fill gas. The procedure for preparing a tank of NF_3 dosed gas is outlined in Section 11.0

10.16.2 Equipment Construction Materials

Nitrogen trifluoride may be handled in glass, stainless steel, copper, monel, or nickel at temperatures up to 200°C. Only nickel and monel are recommended for higher temperatures. However, the process equipment must be scrupulously cleaned to remove such contaminants as dirt, moisture, oil, grease, slag and pipe dope and should be passivated with fluorine before contact with nitrogen trifluoride.

10.16.3 NF_3 Lamp and Cycle Data

The lamp data would be same as expected for $CBrF_3$. A partial pressure of oxygen would also be required for same reasons as with $CBrF_3$.

10.17 MIXED DOSE COMPOSITIONS

There is nothing sacred about having only one type halogen in a lamp. The use of two or more halogens can have lamp performance benefits. The temperature of thermal decomposition increases from Iodine to Fluorine. The higher the thermal decomposition temperature, the greater the chance that tungsten will be deposited on the hottest part of the filament. The affinity of the halogen to form compounds with hydrogen increases from Iodine to Fluorine. This means that free fluorine will react with free hydrogen more readily than will the other halogens. Chlorine will react faster than bromine, etc. All of the halogens seem to need some oxygen available to function properly. To generalize, a fluorine cycle is desirable at the filament and in inert halogen compound near the bulb wall and cool leads and supports is desirable. A combination of carbon, hydrogen, oxygen, iodine, bromine, chlorine and fluorine in whole or in parts may have better properties than any single type halogen dose.

The mixed dose can be a compound such as CH_2BrCl or simply a tank with partial pressure of both CH_2Br_2 and CH_2Cl_2 or $CHBr_3$ and $CHCl_3$ or any other combination.

The following are examples of mixed doses.

BROMOCHLOROMETHANE — CHEMICAL FORMULA CH_2BrCl

This compound has a vapor pressure such that a partial tank pressure of 90 Torr is reasonable. This is about 3 times higher than CH_2Br_2.

TUNGSTEN TRANSFER REACTIONS

$$6CH_2BrCl \longrightarrow 6C + 12H + 6Br + 6Cl$$

$$2W + 6C + 12H + 6Br + 6Cl \longrightarrow WBr_6 + WCl_6 + 12H + 6C$$

$$WBr_6 + WCl_6 + 12H + 6C \longrightarrow 2W + 6HBr + 6HCl + 6C$$

Therefore, in the lamp the cycle is HBr and HCl. These two materials are advantages in the lamp, but not in the equipment.

10.17.1 Halogen Lamp and Cycle Data

A typical gas mixture would be Krypton and 0.45% by volume CH_2BrCl.

In a practical example, a photolamp of 1000 watts at 225 volts with a color temperature of 3400°K, the gas filling consisting of 700 Torr Ar plus 8% by volume of N_2 plus 1% by volume of CH_2Br_2 may be replaced by 700 Torr Ar plus 8% by volume of N_2 plus 0.5% by volume of CH_2BrCl. A lower partial halogen pressure built up from chlorine and bromine in the ration 1:1 thus is sufficient to maintain the cycle while the luminous efficiency of the lamp of approximately 32 lm/w and the lifetime of approximately 30 hours are at least maintained.

This type dose mixture has interesting possibilities for vertically burned linear lamps where gas separation often occurs. It would be possible to have a chlorine cycle at one end, a bromine cycle at the other end and both cycles working in the middle.

10.17.2 Hydrogen Bromine and Carbon Tetrachloride

$$6HBr + 3CCl_4 \longrightarrow 6H + 6Br + 3C + 12Cl$$

$$3W + 6H + 6Br + 12Cl + 3C \longrightarrow WBr_6 + 2WCl_6 + 6H + 3C$$

$$WBr_6 + 2WCl_6 + 6H \longrightarrow 3W + 6Br + 12Cl + 6H$$

$$3W + 6BrH_2Cl + 6H \longrightarrow 3W + 6HCl + 6Br + 6Cl$$

There is not enough hydrogen. There can be two possible results.

A. A short life clean lamp which failed at leads or supports.

B. If there was some water present, the hydrogen would be gettered by the excess Br and Cl.

$$6Br + 6Cl + 6H_2O \longrightarrow 6Br + 6Cl + 12H + 6O$$

$$6Br + 6Cl + 12H + 6O \longrightarrow 6HBr + 6HCl + 3O_2$$

If the dose was 0.5% partial pressure, this is equivalent to 5000 ppm and could getter a considerable amount of water vapor. Of course, the oxygen also has to be gettered. The carbon released from decomposition of the CCl_4 would compound with oxygen to form CO and CO_2.

In other words, this HBr + CCl_4 mixture could be advantageous in a lamp which had a water cycle problem due to bulb outgassing, etc.

10.17.3 CH_2Br_2 + CH_2Cl_2

This mixture would be expected to react the same as CH_2BrCl.

$CHBr_3 + CHCl_3 \longrightarrow 2C + 2H + 3Br + 3Cl$

This mixture would be similar to HBr + CCl_4. That is additional hydrogen is required -- either from lamp impurities or added as H_2 to dose.

$$CHBr_3 + CHCl_3 + 2H_2 \longrightarrow 2C + 6H + 3Br + 3Cl$$

$$2C + 6H + 3Br + 3Cl \longrightarrow 2C + 3HBr + 3HCl$$

10.17.4 CH_3Br + CHI_3

$CH_3Br + CHI_3 \longrightarrow 2C + 4H + Br + 3I$

The Iodine does not need hydrogen, so there is an excess of hydrogen. This material might be good for a long-life lamp because some of the hydrogen would be retained as HI and some lost by permeation. Over a long period there should still be enough hydrogen to eliminate any free Br at wall and leads.

10.17.5 HBr + HI

$HBr + Hi \longrightarrow 2H + Br + I$

This mixture should be good for long-life lamps because the HI will give up the hydrogen and some hydrogen will be lost by permeation. The net result should be a 1:1 ration of Br and H for a longer time than a regular HBr lamp.

10.17.6 Difluorodibromomethane Chemical Formula CF_2Br_2

$$2CF_2Br_2 \xrightarrow{> 2000°C} CF_4 + CBr_4$$

The resulting CF_4 may then dissociate forming

$$2CF_4 \rightleftharpoons C_2F_6 + 2F$$

However, another disproportionation appears to be possible also:

$$2CF_2Br_2 \rightleftharpoons CFBr_2 + CF_3Br$$

with the ensuing reactions under formation of perhalogenated ethanes and of elementary halogens:

$$2CFBr_3 \rightleftharpoons C_2F_2Br_4 + 2Br$$

and

$$2CF_3Br \rightleftharpoons C_2F_4Br_2 + 2F$$

or

$$2CF_3Br \rightleftharpoons C_2F_6 + Br$$

CF_2Br_2 is a stable, non toxic compound that can be admixed to the inert fill gas in the required quantity without any technical difficulties.

It is indicated that there are two transput systems with this compound.

A. A Tungsten-Fluorine cycle close to the filament.

B. A Tungsten-Bromine cycle at cooler parts of filament and mount.

It has been reported that there is no attack of the bulb, leads and supports.

The regeneration of the chemically and thermally stable perhalogenated hydrocarbons from the transient dissociation products is apparently rapid and complete.

10.17.7 Other possible compounds of this type include:

Trifluoromonechloromethane	CF_3Cl
Trifluoromonobromomethane	CF_3Br
Monofluorotribromomethane	CF_3Br
Tetrofluorodibromoethane	$C_2F_4Br_2$
Trifluorotrichloroethone	$C_2F_3Cl_3$

10.18 SOLID MATERIAL DOSING

There are halides suitable for halogen lamp dosing which have too low a vapor pressure to be mixed with the fill gas in a gaseous form or dispersed like iodine from a heated chamber. These halides are stable at room temperature. However, they can be dissociated into their elements by heating within the lamp envelope by lamp operation. The materials are usually phosphonitrilic halides or phosphour tribromide (PBr_3). The halides can be dissolved in inert solvents, preferably non-polar solvents such as benzene, ether, petroleum ether and chlorinated hydrocarbons and can thus be introduced into the lamp envelope as a solution by injection onto the filament or envelope wall. The solvent can be evaporated from the envelope, e.g., under a vacuum, leaving the halide as a residue.

10.18.1 Phosphonitrilic Halides (B-1)

These materials are halides having different halogen atoms and/or different number of (PNY_2) units where Y is the halogen in the molecule. These molecules include:

$(PNBr_2)_3$
$(PNBr_2)_4$
$(PNCl_2)_4$
$(PNCl_2)_5$
$(PNCl_2)_6$
$(PNCl_2)_7$

It should be noted that since these materials are dispersed at beginning of exhaust cycle, the exhaust cycle is a cold cycle. That is the lamp cannot be heated to any appreciable degree or the halide will varporize and be removed from the lamp.

For additional in-depth data, see U.S. Patent #3,712,701 (1973) issued to British Lighting Industries (Thorn).

10.18.2 Phosphorus-Bromine-Hydrogen

$P_3N_4H_2Br_5$ and/or $P_3N_5H_4Br_4$

This material is similar to 10.18.1 with the addition of hydrogen. It has been claimed that phosphorus is not an effective binder of bromine and that as a result of this a quantity of $(PNBr_2)_n$ lying within narrow limits must be dosed to obtain a readily operating lamp: when the dose is too small, the lamp vessel will blacken; when the dose is too high, the end of life of the lamp is reached as a result of attack of the colder tungsten parts. When $(PNBr_2)_n$ is used, readily operating lamps can be manufactured only if highly loaded and hence short-life lamps are concerned and the bromine compound is accurately dosed.

This material when decomposed yields HBr + nitrogen + phosphorus.

The recommended solvents for lamp dosing are benzene, toluene, petroleum ether/or acetonitrile.

Lamp Manufacturing Data (12V/55W H-1 Headlight Lamp)

Solution: 50mg $P_3N_5H_4Br_4$ in 100 ml of benzene

µg$P_3N_5H_4Br_4$	Life Hr.
10.2	275
17	265
34	180
51	220
85	220
170	> 180

In order to find out the influence of the presence of oxygen on the operation of the tungsten/bromine cycle a number of lamps were manufactured to which 1, 2 or 3 Torr oxygen were added in addition to $P_3N_5H_4Br_4$ and krypton.

µg$P_3N_5H_4Br_4$	Torr O_2	Life Hr.
17	1	240
34	1	320
51	1	280
85	1	285
17	2	290
17	3	275

These experiments prove on the one hand that a large variation in the dosed quantity of the phosphorus hydrobromic acid source is permissible, on the other hand that oxygen is effectively made harmless by the well known Phosphorus oxygen gettering chemistry.

For additional information, see U.S. Patent #4,039,879 (1977) issued to U.S. Philips Corp.

10.18.3 Phosphorus Tribromide (PBr_3)

PBr_3 is unique in that it can be solid dosed in a ether solution or it can be dispensed in a vapor form at low pressures.

VAPOR PRESSURE OF PBr_3

Pressure (Torr)	Temperature (°C)
1	7.8
10	47.8
40	79.0
100	103.6

It has been claimed that in the manufacture of lamps with $(PNBr_2)_x$ it is necessary to carefully remove from the lamp the solvent used for introducing the compound containing phosphorus and bromine into the lamp. In fact, when the solvent is not completely removed, this may give rise to the formation of light-absorbing black carbon deposits on the wall. Such black deposits may absorb so much light and consequently rise in temperature that the walls of the envelope locally weakens and swells. This may result in the premature end of the lifetime of the lamp by perforation of the bulb wall. In addition there have been instances where the solvent on filament resulted in lamp failure due to brittle filaments.

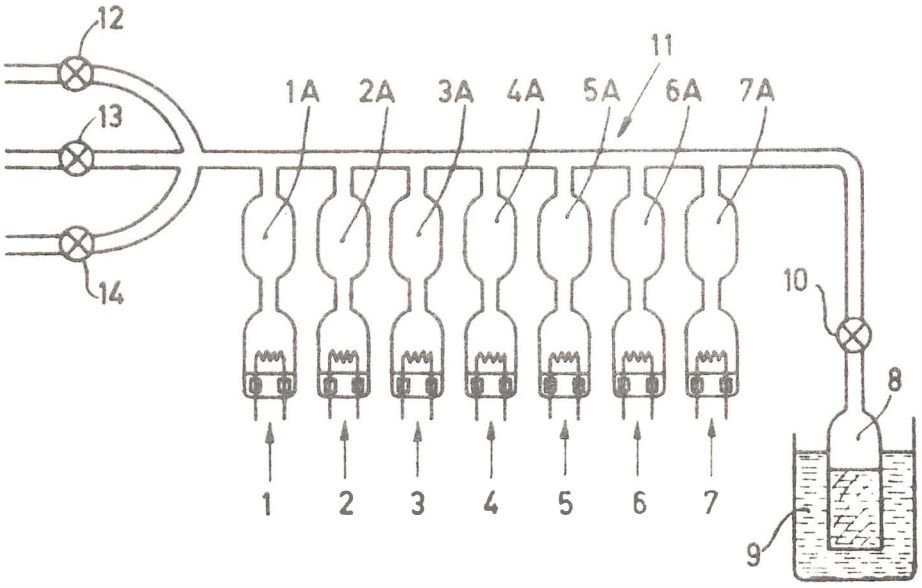
VAPOR DOSING OF PBr_3

The setup comprises a reservoir of liquid phosphorus tribomide. The PBr_3 is immersed in a liquid bath 9 in which the reservoir 8 can be maintained at a constant temperature associated with the desired phosphorus tribromide vapor pressure. The liquid bath may be filled, for example, with water. The reservoir 8 is connected to the duct 11 by means of a valve 10. The lamps 1 to 7 are

connected to this duct 11 over the gas spaces 1A to 7A. Furthermore the duct 11 is connected via three valves 12, 13, and 14 to a vacuum pump, a reservoir having a rinsing gas and a reservoir have a rare gas and/or nitrogen (not shown). The entire arrangement shown may consist of glass.

For filling the lamps 1 to 7 the following operations are carried out:

After the lamps 1 to 7 with the gas spaces 1A to 7A are connected to the duct 11 evacuation is effected up to a pressure of approximately 10^{-4} Torr while keeping the valves 10, 13, and 14 closed and the valve 12 open. Subsequently valve 12 is closed and valve 13 is opened so that the lamps 1-7, the gas spaces 1A-7A and the duct 11 are filled with a rinsing gas, for example, consisting of 92 percent by vol. of N_2 and 8 percent by vol. of H_2. Valve 13 is closed and valve 12 is opened and the lamps 1-7, the gas spaces 1A-7A and the duct 11 are again evacuated (approximately 10^{-4}Torr). This process may be repeated several times. The reservoir 8 is meanwhile brought to the temperature associated with the desired phosphorus tribromide vapor pressure. This temperature is 4°C at 0.5 Torr, 9°C at 1 Torr and 17°C at 2 Torr. The use of a higher pressure than approximately 2 Torr is not desirable because then there is the risk that PBr_3 condenses in the lamps 1-7, the gas spaces 1A-7A or the duct 11. After the lamps 1-7, the gas spaces 1A-7A and the duct 11 have been evacuated for the last time, valve 12 is closed and valve 10 is opened.



LAMP MANUFACTURING RESULTS

The quantities of phosphorus tribromide (indicated in Torr) mentioned in Table 1 below were introduced into cylindrical lamps in which the tungsten filament was located on the axis of the cylinder having a content of approximately 5.8 cubic cms (225 volt, 1000 Watt, 21 lm/Watt). Argon was added until the total pressure was 2.5 atmospheres.

TABLE I

Filling Pressure PBr_3 in Torr	Results
0.8	Lamps blacken after a short period of operation
2	Sometimes light blackening after a comparatively long period of operation
3	No blackening until the end of the lifetime average lifetime approximately 3000 hours
4	Likewise as with 3 Torr PBr_3 filling
6	Average lifetime decreases to approximately 1500 hours due to filament attack.

For additional information see:

1. U.S. Patent #3,800,180 (1974) issued to DeFraeye et al. (Netherlands)
2. Studies on New Type Mine Lamp, Fundan University, Shanghai, China, Published in IEEE 1980 (CH1575-0/80/0000-1244)
3. Japan Patent #48-12156 (1973)

10.18.4 Copper Bromide $CuBr_2$

One of the assets of $CuBr_2$ as a dosing material is that it is non-poisonous.

The $CuBr_2$ is soluble in a volatile hydrocarbon such as ethyl alcohol.

Unlike other solid dose materials, the $CuBr_2$ is applied by dipping the filament before sealing like present application of phosphorus in GLS lamp manufacturing. However, it is necessary that the shortest distance to seal must be greater than 20 mm for quartz tubular lamps.

The recommended solution is 0.35 to 0.38 grams of copper bromide per 100 ml of ethyl alcohol (C_2H_5OH). After dipping, the ethyl alcohol evaporates leaving a uniform coating of copper bromide adhered to the filament. When the halogen lamp is energized, the copper bromide vaporizes and dissociates into copper and bromine.

It has been claimed that good lamps can be made with no exhaust process. That is, the lamp is complete after press seal like a cartridge lamp or tipless halogen lamp as made by Winchester.

For further information, see German Patent #DE 28 03 122 (1979) issued to Honau Quarzlampen GmbH.

10.19 LINEAR HALOGEN PRODUCTION LAMPS WITH VARIOUS HALOGEN DOSE COMPOSITIONS

TH LINEAR LAMPS THAT ARE KNOWN TO OPERATE SATISFACTORILY WITH GAS FILLING 0.05% CH_2Br_2 BALANCE Ar + IODINE

VOLTS	WATTS	LUMINOUS FLUX (LUMENS)	EFFICIENCY (LUMENS PER WATT)	COLOR TEMP (DEG K)	COLD FILL PRESSURE (ATMOSPHERES)	VOLUME (CM^3)	LAMP LENGTH (MM)	LIFE (H)	TYPE OF FILAMENT
225,245	750	14800	19.7	2900	2-2 1/2	8.0	178	2000	SC
120	750	15000	20.0	3000	2-2 1/2	8.5	189	2000	SC
225,245	750	14800	19.7	2900	2-2 1/2	8.5	189	2000	SC
120	1000	21000	21.0	3000	2-2 1/2	8.5	189	2000	SC
225,245	1000	21000	21.0	3000	2-2 1/2	8.5	189	2000	SC
225,245	1500	31500	21.0	3000	2 1/2-3	12.0	254	2000	SC
225,245	2000	45000	22.5	3100	2 1/2-3	16.5	333	2000	SC
225,245	2000	45000	22.5	3100	2 1/2-3	18.0	307	2000	SC

TH LINEAR LAMP KNOWN TO WORK SATISFACTORILY USING 0.35% CH_2Br_2 BALANCE N_2

225,245	800	20800	26.0	3200	1-1 1/2	3.0	78	75	CC

TH LINEAR LAMPS KNOWN TO PERFORM SATISFACTORILY USING 0.5% HBr, 4.5% N_2 BALANCE Ar

120	1000	27000	27.0	3200	1-1 1/2	8.5	189	150	SC
225,245	1000	26500	26.5	3200	1-1 1/2	8.5	188	150	SC
225,245	625	16000	25.6	3200	1-1 1/2	8.5	189	200	SC
225,245	1250	34000	27.2	3200	1-1 1/2	8.5	189	150	SC
225,245	625	17000	27.2	3200	1 1/2-2 1/4	4.0	117	75	CC
225,245	800	20500	26.7	3200	2-2 1/2	4.0	117	150	CC

TH LINEAR LAMPS KNOWN TO OPERATE SATISFACTORILY USING GAS FILLING 1% HBr BALANCE N_2

120	650	17550	27.0	3200	1-1 1/4	3.0	78	100	CC
120	420	11340	27.0	3200	1-1 1/4	2.2	63	75	CC
120	650	21450	33.0	3400	1-1 1/4	3.0	78	12	CC
225,245	800	23200	29.0	3400	1-1 1/2	3.0	78	12	CC
225,245	1000	33000	33.0	3400	1-1 1/2	4.5	127	12	SC
225,245	1250	41250	33.0	3400	1-1 1/2	4.5	127	12	SC

TH LINEAR LAMPS KNOWN TO OPERATE SATISFACTORILY USING 2% HBr BALANCE N_2

120	600	16500	27.5	3200	1-1 1/4	3.0	93	75	CC
225,245	600	16200	27.0	3200	1-1 1/4	3.0	93	60	CC
30	250	8250	33.0	3400	1.0	2.4	78	12	SC

10.20 Tungsten Halogen Identification

Some of the halogen compounds in lamps can be identified by color. The following table shows some of the possible compounds and distinctive colors.

COLOR	COMPOUND	FORMULA	NOTES
Black	Tungsten tetraiodide	WI_4	Caused by puffing (1st)
	Tungsten oxytetrabromide	$WOBr_4$	
	Nitrogen tri-iodide	NI_3	
Gray-Black	Tungsten Metal	W	Coil material
Blue-Black	Tungsten dibromide	WBr_2	Caused by coil attack
	Tungsten hexabromide	WBr_6	Caused by coil attack
Violet-Brown	Tungsten pentabromide	WBr_5	Caused by coil attack
Gray-Grown	Tungsten di-iodide	WI_2	Caused by coil attack
Dark Brown	Nitrosyl bromide	NOBr	
	Bromine monoxide	Br_2O	Created during burning
Brown	Tungsten dioxide	WO_2	Coil oxidation
	Tungsten dinitride	WN_2	
Blue-violet	Tungsten pentoxide	W_2O_5 (or W_4O_{11})	Coil oxidation
	Nitrous Anhydride	N_2O_3	Created during burning
Blue	Nitrogen trioxide	NO_3	Normal result in O_2 lamps
Bluish	Tungsten oxydibromide	WO_2Br_2	
Red	Bromine hydrate (degree of red depneds upon x, which varies from 1 to 10)	$Br_2 - x\ H_2O$	Water vapor in lamp
	Iodine dioxide	IO_2	
Lemon-Yellow	Di-iodide tetraoxide	I_2O_4	
	Tetraiodide nonoxide	I_4O_9	
Yellow	Tungsten trioxide	WO_3	Coil oxidation
	Tungstic Acid	H_2WO_4	Usually caused by leaks
Light Yellow	Bromine dioxide	BrO_2	Normal result to burning
White	Iodide pentoxide	I_2O_5	
	Tribromide octoxide	$(Br_3O_8)_n$	Normal result in O_2 lamps
	Nitric Anhydride	N_2O_5	

This list is not to be used as a listing of causes, but is to serve only as an indicator of the materials involved when a problem does arrive. No conclusion should be reached from coloration only - all preliminary conclusions should have a complete check, through tests, measurements and analysis.

10.21 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

1. Method of Dosing an Incandescent Lamp with a Controlled Amount of Halogen Containing Material. Westinghouse U.S. Patent #3,788,725 (1974).

11.0 THE FILL GAS MIXING STATION

The mixing station should be in a room by itself. There should be safe storage area for the tanks of dose gases. Most of these gases are very toxic. Gas Mask and shower heads should be available and in workable conditions at all times.

NOTE: Be extremely cautious not to mix air or O_2 with CO, H_2, or CH_4. Take no risks with high pressure cylinders even if filled with inert gas. If a high pressure cylinder is damaged it may accelerate to a high velocity and do much damage as the escaping gas jet is powerful.

The room should have a vent and blower to the outside to change air in room quickly if necessary. The air removed from the room by blower should be directed away from any other windows, etc., above roof would be preferable.

The dose supply tank in use should be near floor and in a box that is ventilated to outside. Most dose gases are heavier than air.

11.1 GAS MIXING INSTRUCTIONS MULTIPLE HALOGEN STATION

1. The gas mixing station described in this specification has two manifolds, one used for mixing and one which is under constant vacuum (see Figure 1a) the schematic and look at the back of the mixing station. All of the ball valves have three positions with the exceptions of the ball valve on the flexible hose and the one connecting the mixing and vacuum manifolds, which only turn on and off. With the handle horizontal the three position ball valves are off; when pointing towards the mixing manifold they connect to the mixing manifold; and when pointed in the opposite direction they connect to the vacuum manifold (see Fig.1a, b, c). Each of these valves will connect either a gas cylinder or a gauge to the chosen manifold. Several of the gases more commonly used at low percentages also have a metering valve in the line in order to slow down the gas flow and ease mixing.

A. Equipment

1. Vacuum pump with Edwards #18 vacuum oil, or equal.
2. Absolute pressure gage in millimeters.

3. Manifold and associated valves and piping for containing hydrogen bromide.
4. Manifold and associated piping, valves and gages to contain and measure the carrier gas.
5. Thermocouple gage and meter.
6. Regulators for carrier gas and hydrogen bromide pressure regulation.
7. Tank containing water and ammonium hydroxide pellets.
8. Monel tank to contain halogen and carrier gas mixture with pressure gage and shut off valve.
9. Psig gages.

II. MATERIALS

Use material shown for specific mix by part number (5750-SERIES).

III. PROCEDURES (FIGURES FOLLOW THE TEXT OF THIS SPECIFICATION)

A. PUMPING DOWN A TANK

1. Close all valves and read the thermocouple gauge to be sure the system is holding a vacuum.
2. Take a tank which has already been rough pumped, connect it to the flexible hose, and open the valve connecting the two manifolds (Figure 2 step 1).
3. Open the valve at the end of the flexible hose (Figure 2 step 2) in order to pump the air out of the line.
4. Open the tank valve and read the tank vacuum on the thermocouple gauge (Figure 2 steps 3 & 4) 30 microns or less is acceptable. If above 30μ simply wait for the tank to pump down.
5. Open the valves to the gauges to pump the lines down (Figure 2 , steps 5, 6, 7 & 8). Thenclose the valve to the 0-500 mm and 0-800 mm gauges.

B. MAKING A GAS MIX (FOR DETAILS SEE SPEC. 10B0707-0047)

Example is AN 11 with 0.3% O_2 added. Fill to 18.57 mm with O_2 to 53.47 mm with HBr, to 22.4 psig with N_2, and to 105 psig with Ar. Low percentage gases are added first so they can be measured with the 0-500 mm gauge and O_2 is added before HBr as there is no metering valve on the O_2 line, making it difficult to control the amount added. If too much O_2 is inadvertently put in, the excess can be pumped out as it is the only gas in the system.

1. Adding O_2

   a. Close the valve connecting the two manifolds (Figure 3 step 1).

   b. Add some O_2 by opening and closing the O_2 valve (Figure 3 step 2) to the mixing manifold.

   c. Connect the 0-500 mm gauge by opening the appropriate ball valve and slowly opening the shut-off valve (Figure 3 steps 3 & 4). Note: This must be done carefully as the 0-500 mm gauge is easily damaged by overpressure.

   d. If there's insufficient pressure, shut off the 0-500 mm gauge and repeat the above process. On the other hand, in the event of too much pressure open the valve connecting the two manifolds and pump the surplus O_2 out.

2. Adding HBr

   a. Open 0-500 mm gauge's ball and shut-off valves (Figure 4 steps 1 & 2)

   b. HBr shut-off and metering valves are opened (Figure 4 steps 3, 4 & 5)

   c. Add HBr by intermittent use of the toggle valve (Figure 4 step 6) until 63.57 mm is reached.

   d. Shut off HBr (Figure 5 steps 1 & 2)

3. Adding Nitrogen

   a. Shut off the 0-500 mm gauge (Figure 5 steps 3 & 4) as the high pressure will ruin it.

   b. Add N_2 by turning the N_2 ball valve toward the mixing manifold (Figure 5 step 5) until the pressure shown is 22.07 psig.

   c. Allow the tank to sit for a time, as gas addition heats the tank, often causing a false pressure reading. Add more N_2 until the tank stabilizes at the desired pressure.

4. Adding Argon

   a. Add Ar in the same manner as N_2. Fill to 105 psig. (Figure 6)

C. DISCONNECTING A TANK

1. Shut off the tank valve (Figure step 1)

2. Open up the valve connecting the two manifolds (Figure 7 step 2). Open it partially and pump slowly to reduce strain on the vacuum pump until the pressure drops to 0 on the 0-150 psig gauge.

3. Turn off the valve at the end of the flexible hose (Figure 7 step 3).
4. Disconnect the tank.
5. Open the valves to the 0-500 mm gauge (Figure 7 steps 4, 5) to pump down the gauge line.
6. Open the toggle valve (Figure 7 step 7) to pump down the HBr line.
7. Close the toggle valve, then shut off the appropriate valves to the 0-500 mm gauge.
8. Another tank may now be connected.

IV. SPECIAL PRECAUTIONS AND SAFETY

A. Be very cautious with the 0-500 mm and 0-800 mm gauges as they are easily damaged by too much pressure.

B. Be extremely careful when working with flammable gases, such as H_2 and Methane. NEVER ADMIT OXIDIZING AGENTS SUCH AS O_2, CARBON MONOXIDE, AND AIR.

C. SAFETY PRECAUTIONS AND HANDLING

1. Vent vacuum pump to outside.
2. Ensure that all connections are tight and that "O" rings are replaced in monel tank fittings as required.
3. All pressurized Monel Tanks shall be capped when not in use.
4. Observe all handling and safety precautions as posted in the area where subject procedure is carried out.
5. When dumping gas from a tank that is to be refilled, connect line from water tank to gas tank. Open gas tank valve, open valves on flexible line. When pressure on tank gauge drops to zero, reverse the order, above. (i.e., close faucets to tanks - close gas tank valve.)

V. INSPECTION

A. Make lamps from subject hydrogen bromide/gas mixture and evaluate lamp performance before tank is released for production.

VI. MAINTENANCE

If any difficulty is found in pumping the system down, there's

a good chance that the problem is; outgassing. The mixing manifold may be filled with nitrogen and pumped down a few times to remove the offending contaminant. If a good enough vacuum still can't be had, a leak must be searched for.

NOTE: "OUTGASSING" is caused by the presence in the system of a material which has a low vapor pressure. As the system is pumping down the contaminant will slowly change from liquid to vapor, preventing the system from achieving a good vacuum. The addition and pumping out of a high vapor pressure gas like nitrogen will usually eliminate the problem by "sweeping" the contaminant out along with itself. It may take several applications of the "cure" to solve the problem. If there is a leak, the system may be charged with nitrogen and the leak found with "snoopy" a soap solution. If the leak is too small to be found by the bubble method, a veeco leak detector may be connected to the system.

VII. For specific gas mixes, see spec. 10B0707-47 and/or 5750 - part series.

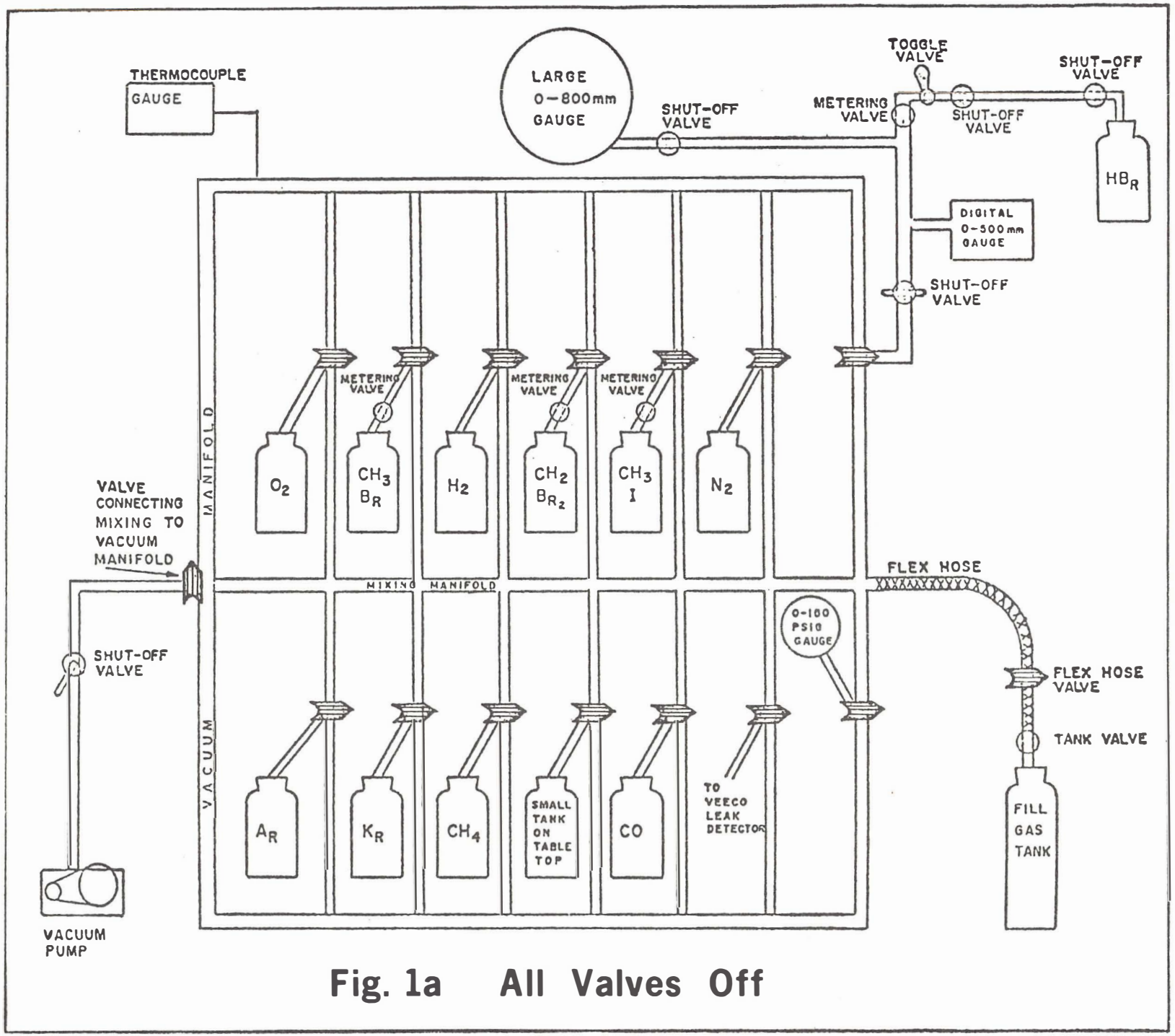


Fig. 1a All Valves Off

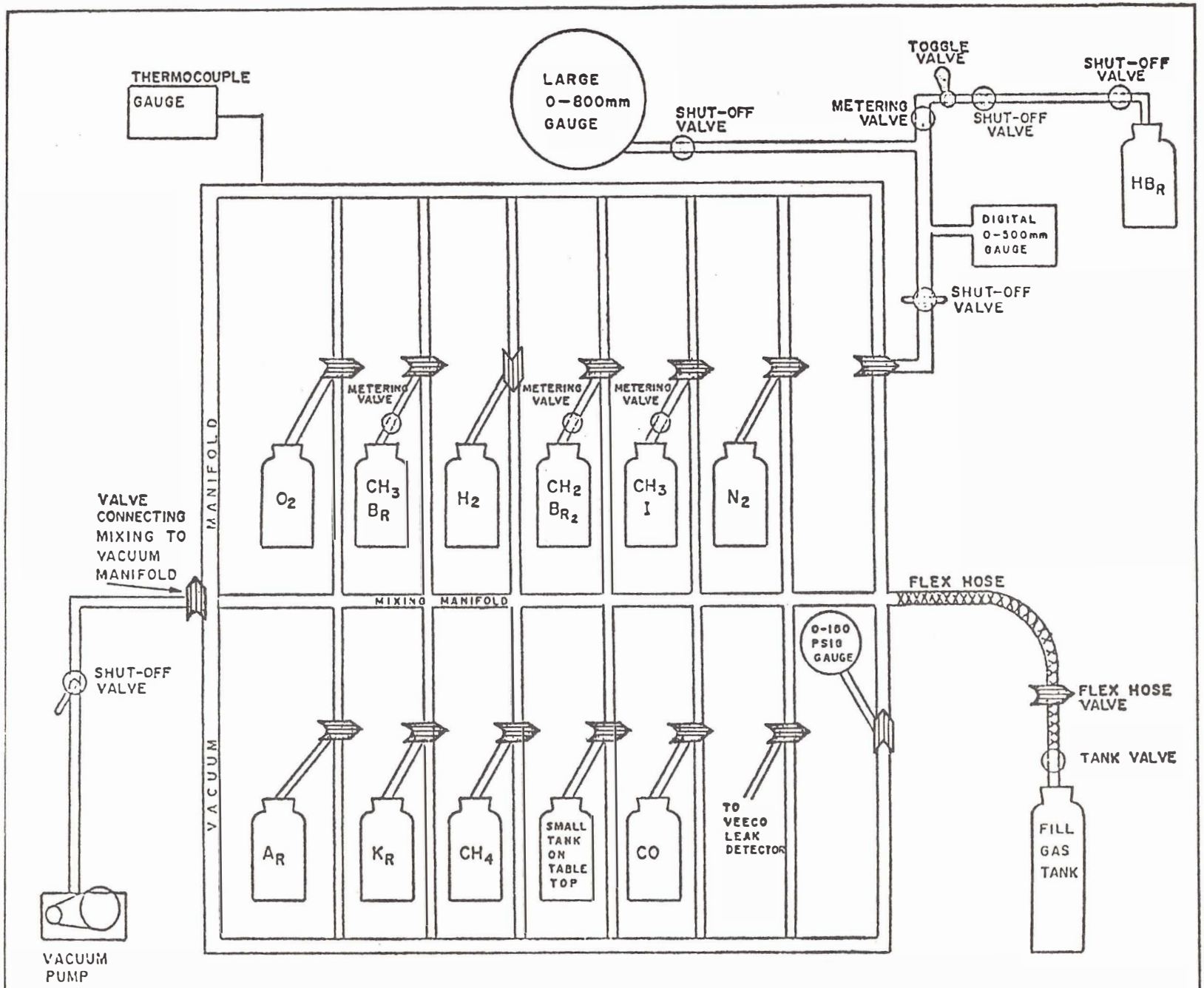


Fig. 1b H_2 and O-150 PSIG Gauge Open to Mix Manifold

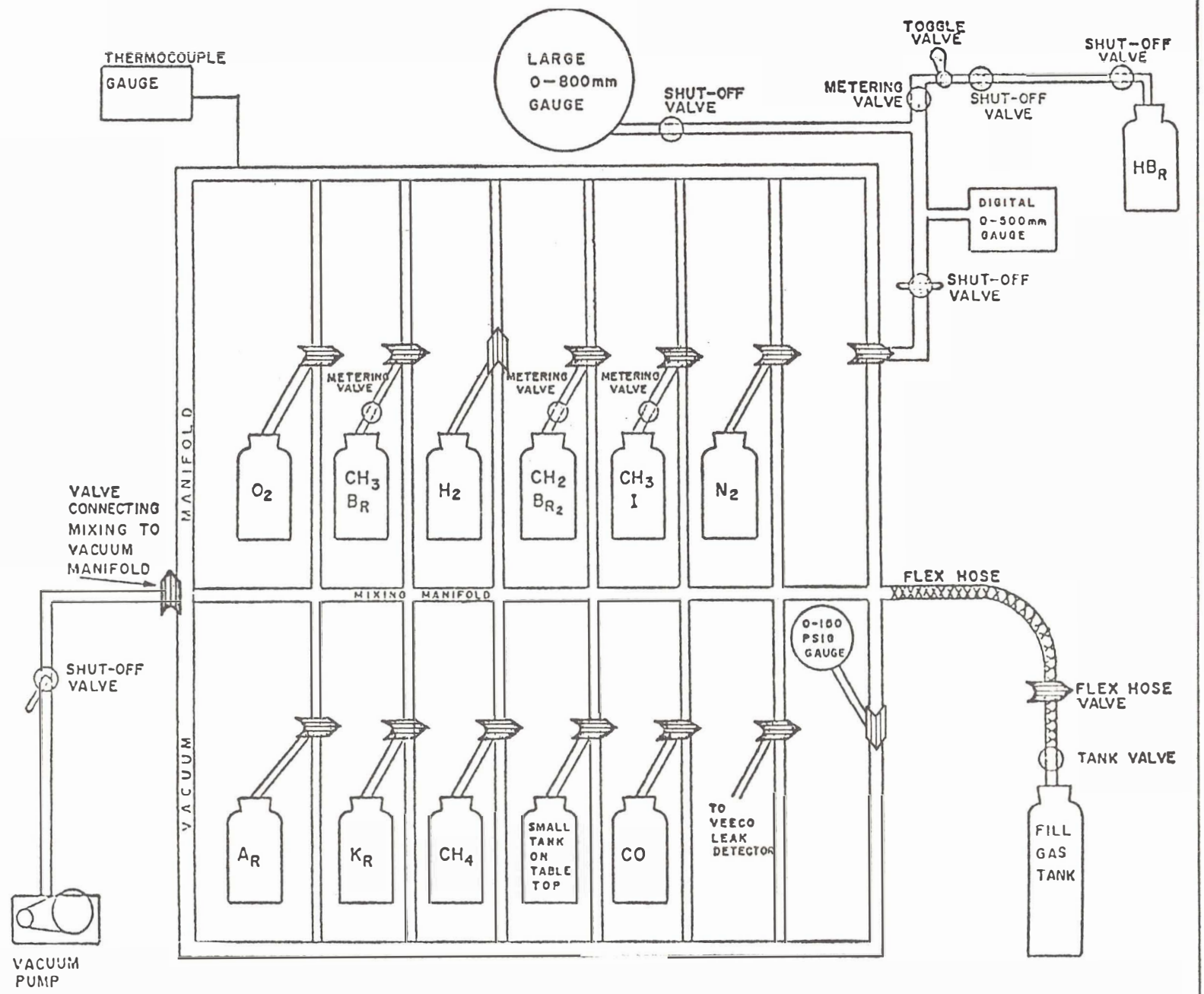


Fig. 1c H_2 and O-150 PSIG Gauge Open to Vacuum Manifold

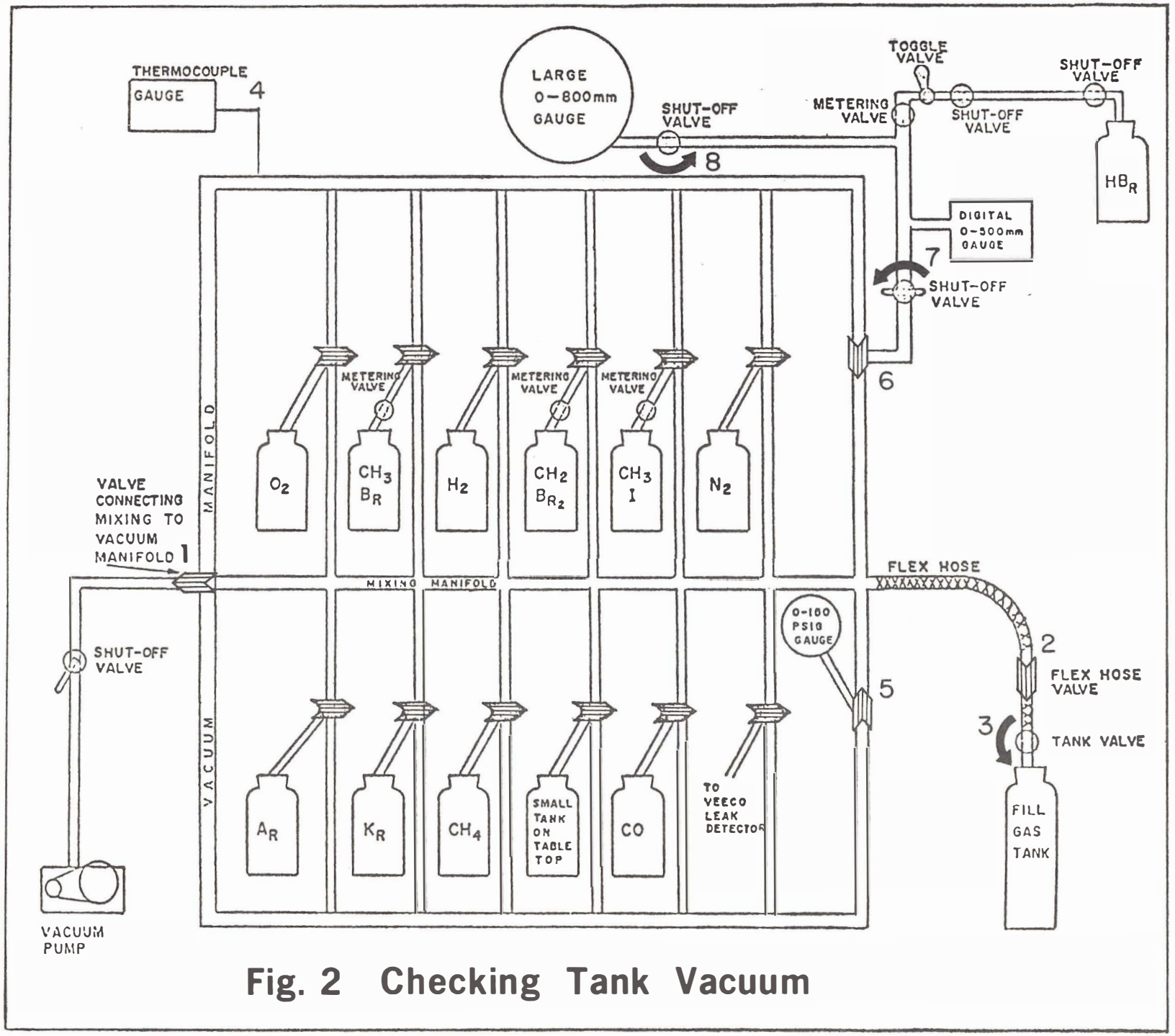


Fig. 2 Checking Tank Vacuum

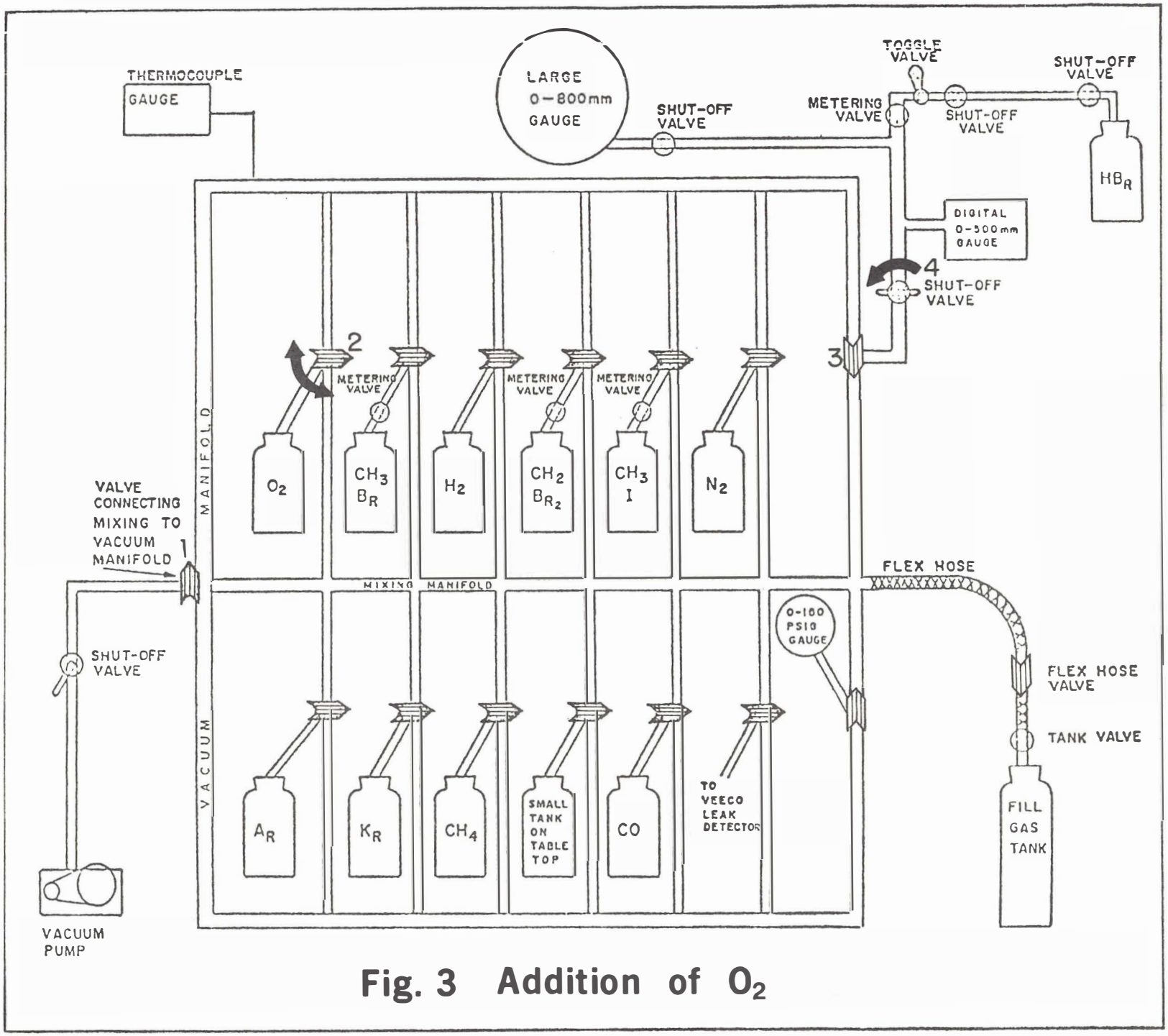


Fig. 3 Addition of O_2

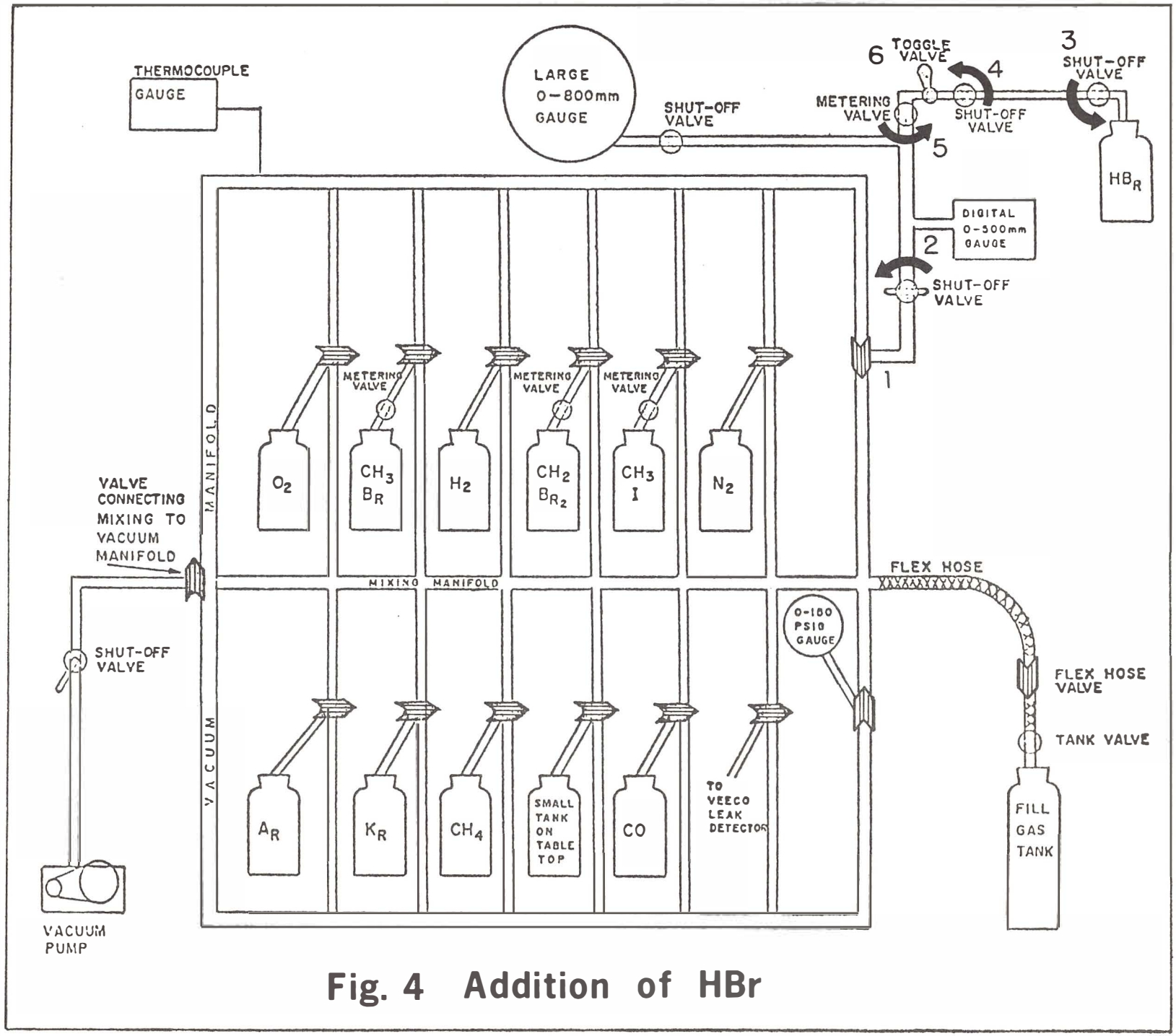


Fig. 4 Addition of HBr

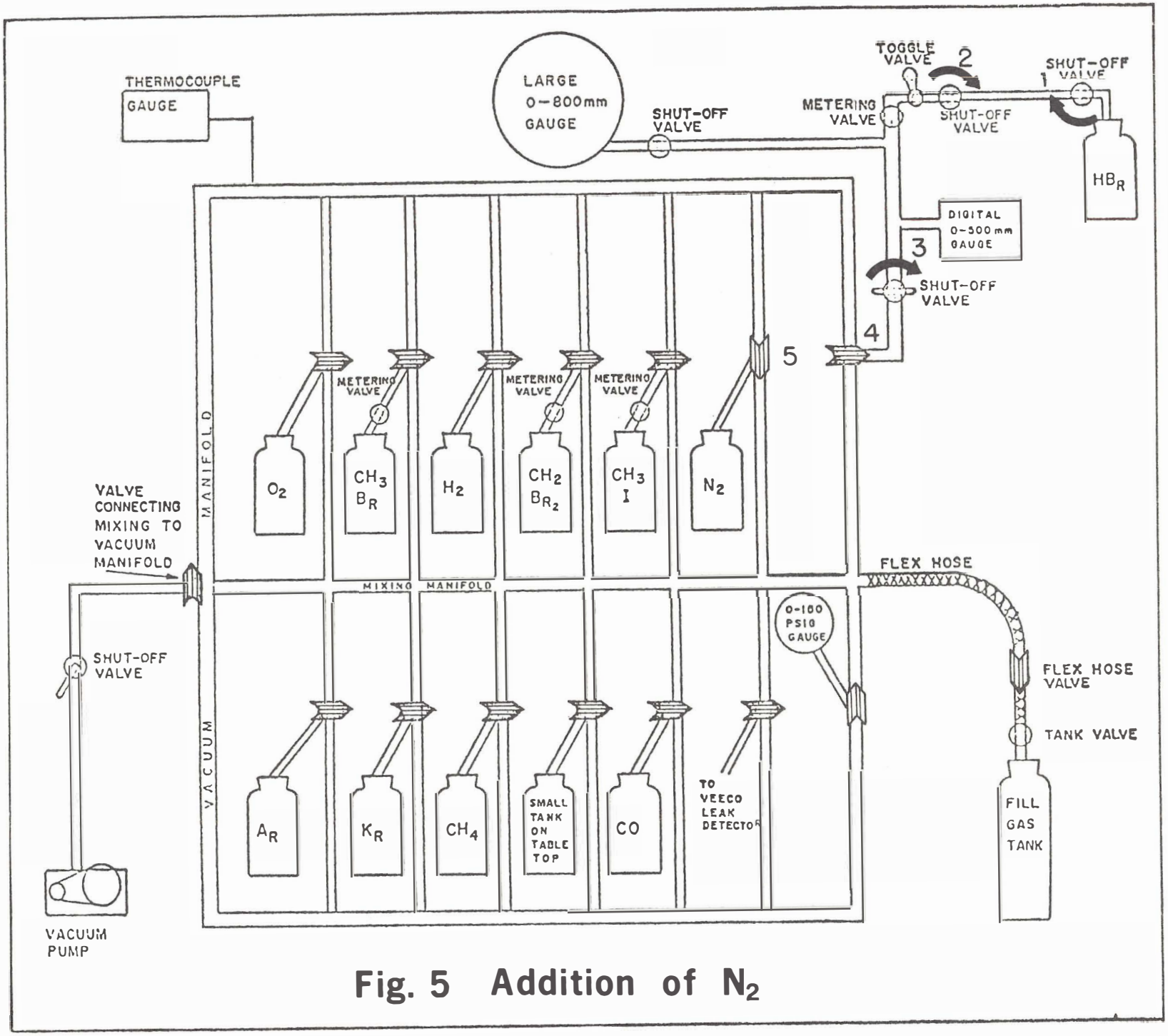


Fig. 5 Addition of N_2

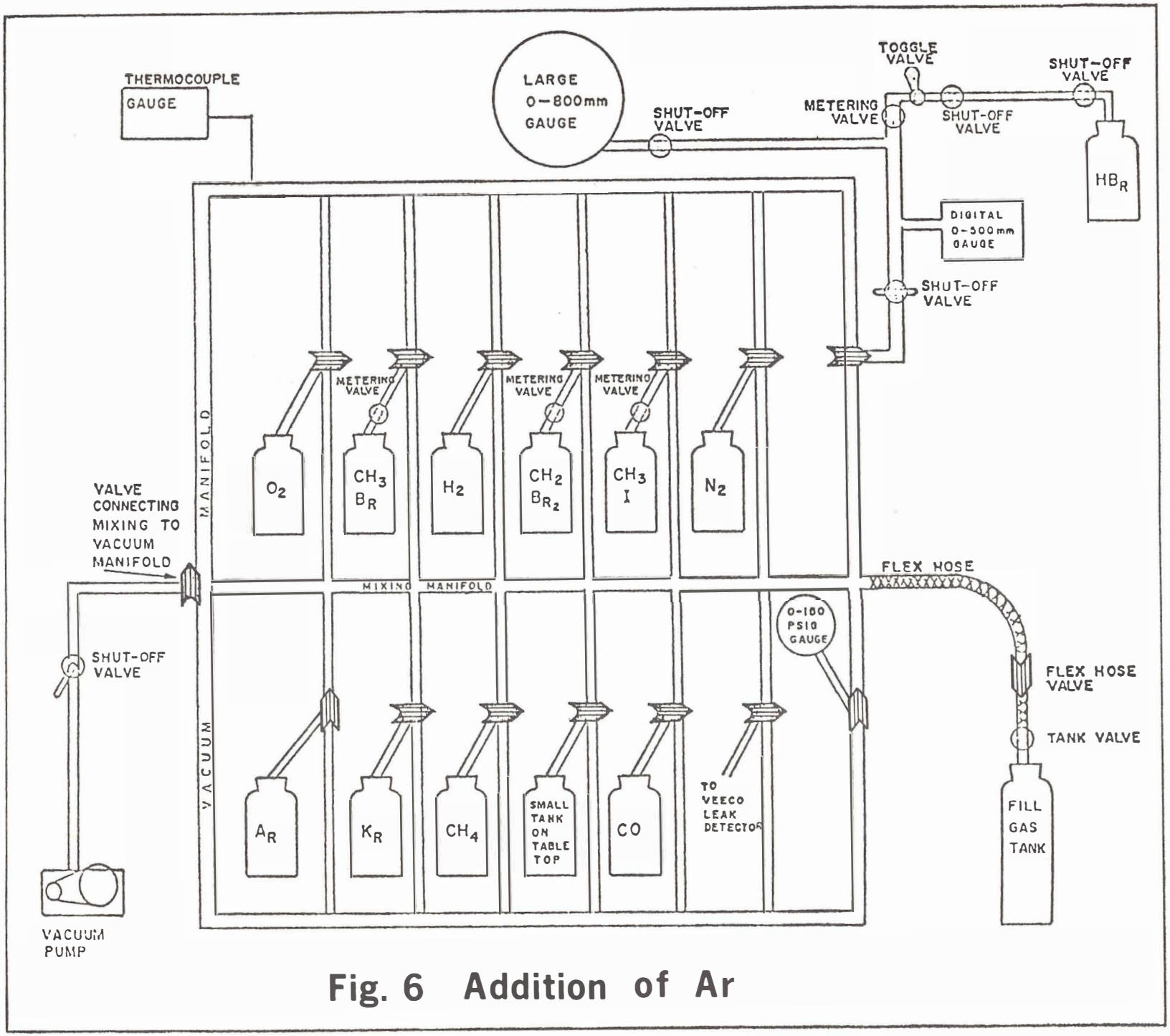


Fig. 6 Addition of Ar

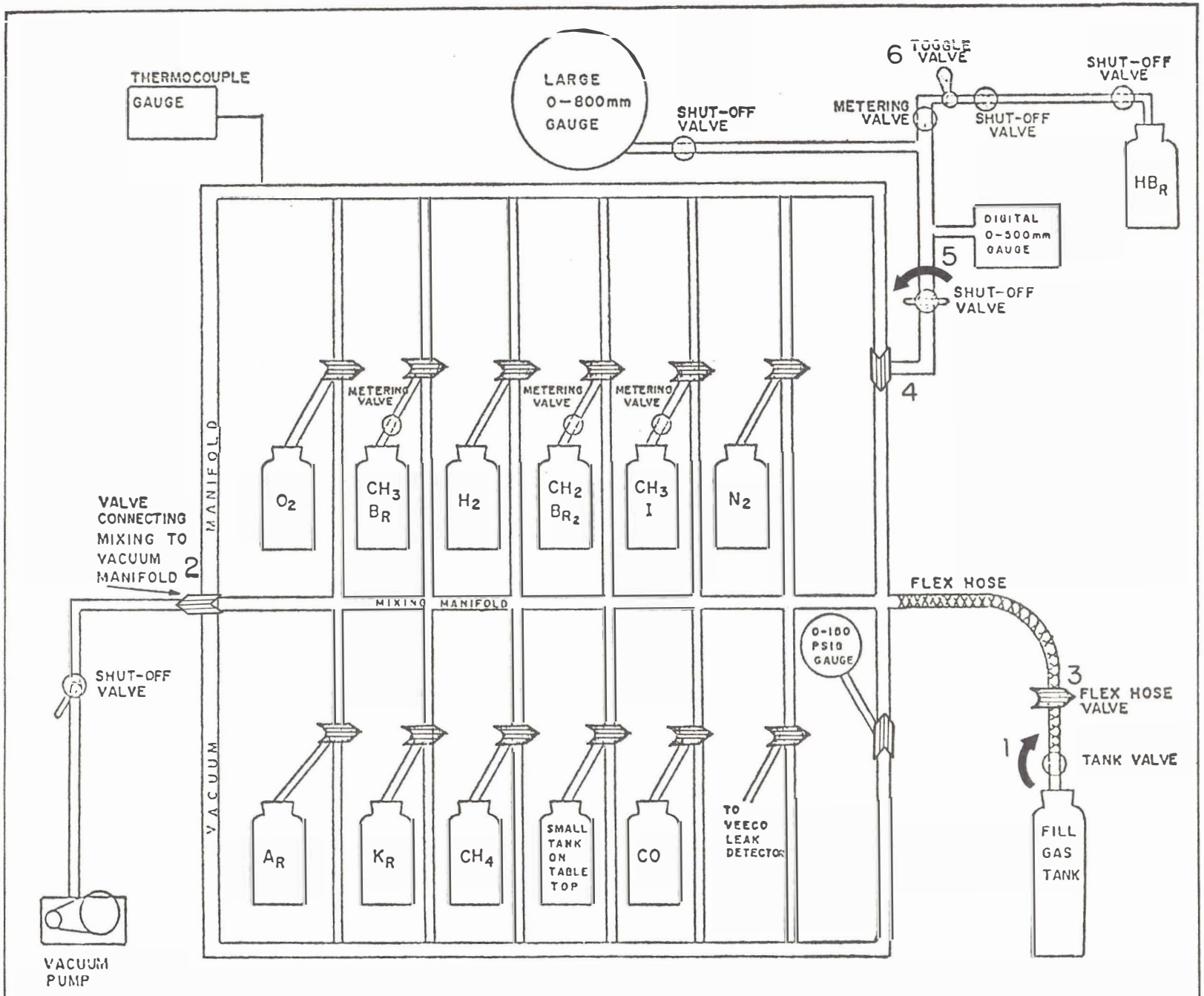


Fig. 7 Tank Removal System Pump Down

11.2 MIXING HYDROGEN BROMIDE (ONLY) IN CARRIER GAS FOR LAMP FILL

I. EQUIPMENT

A. Vacuum pump with Edward's #18 vacuum oil or equal.

B. Absolute pressure gage in millimeters.

C. Manifold and associated valves and piping for containing Hydrogen Bromide.

D. Manifold and associated piping, valves and gages to contain and measure the carrier gas.

E. Thermocouple gage and meter.

F. Regulators for carrier gas and Hydrogen Bromide pressure regulation.

G. Reservoir containing water and ammonion hydroxide pellets.

H. Monel tank to contain hydrogen bromide and carrier gas mixture with pressure gage and shut-off valve.

II. MATERIALS

A. As shown on material list for given gas mix.

III. PROCEDURE

A. Evacuate entire system and monel tank to 30 microns or less. This is with all valves open. (1) Carrier gas regulator valve (2) Valve between high and low pressure side of system (3) Both pump valves (4) Valve to absolute pressure gage, and gage housing (5) Valve to fill gas tank and (6) Valve on the tank itself.

B. With both pump valves closed and the valve to the absolute pressure gage housing closed, admit hydrogen bromide into the system and tank to obtain the proper percentage appropriate for the gas mixture required - as shown on chart. This pressure is monitored on the absolute pressure gage.

C. Close off the valve to the HBr manifold (valve between the high and low sides) and admit carrier gas to manifold and monel tank to the required pressure level.

CAUTION: Failure to close the valve to HBr manifold will admit high pressure gas to the absolute pressure gage - it is delicate and over pressure will ruin it.

D. Let the monel tank cool to room temperature and make final pressure adjustment. Shut off monel tank valve.

E. Close high pressure tank valve. Close valve at the end of line to fill gas tank.

F. Open high pressure vacuum valve slightly, to pump high pressure gas from lines, then open fully to pump down system. When pressure brings thermocouple pointer "back on scale," open the valve to HBr manifold. Open low pressure vacuum valve and open valve to absolute pressure gage housing.

G. Leave entire system pumped down.

IV. INSPECTION

A. Make lamps from subject hydrogen bromide/gas mixture and evaluate lamp performance before tank is released for production.

V. SAFETY PRECAUTIONS AND HANDLING

A. Vent vacuum pump to outside.

B. Ensure that all connections are tight and that "O" rings are replaced in monel tank fittings as required.

C. All pressurized monel tanks shall be capped when not in use.

D. Observe all handling and safety precautions as posted in the area where subject procedure is carried out.

E. When dumping gas from a tank that is to be refilled, connect line from water reservoir to gas tank. Open gas tank valve, open valve on flexible line. When pressure on tank gage drops to zero, reverse the order above.

VI. For specific gas mixes, see spec 10B070-47 and/or 5759-part series.

VII. VALVE IDENTIFICATION FOR DRAWING WHICH FOLLOWS

1. HBr (valve to HBr tank)

2. L.P. gage housing (valve to low pressure gauge housing)

3. L.P. vac. (low pressure side to vacuum pump valve)

4. L.P. valve (low pressure shut off to fill manifold)

5. Fill tank connecting line valve

6. Tank valve (bellows valve on tank)

7. H.P. valve (high pressure shut off to fill manifold)

8. Ar (fill gas line valve)

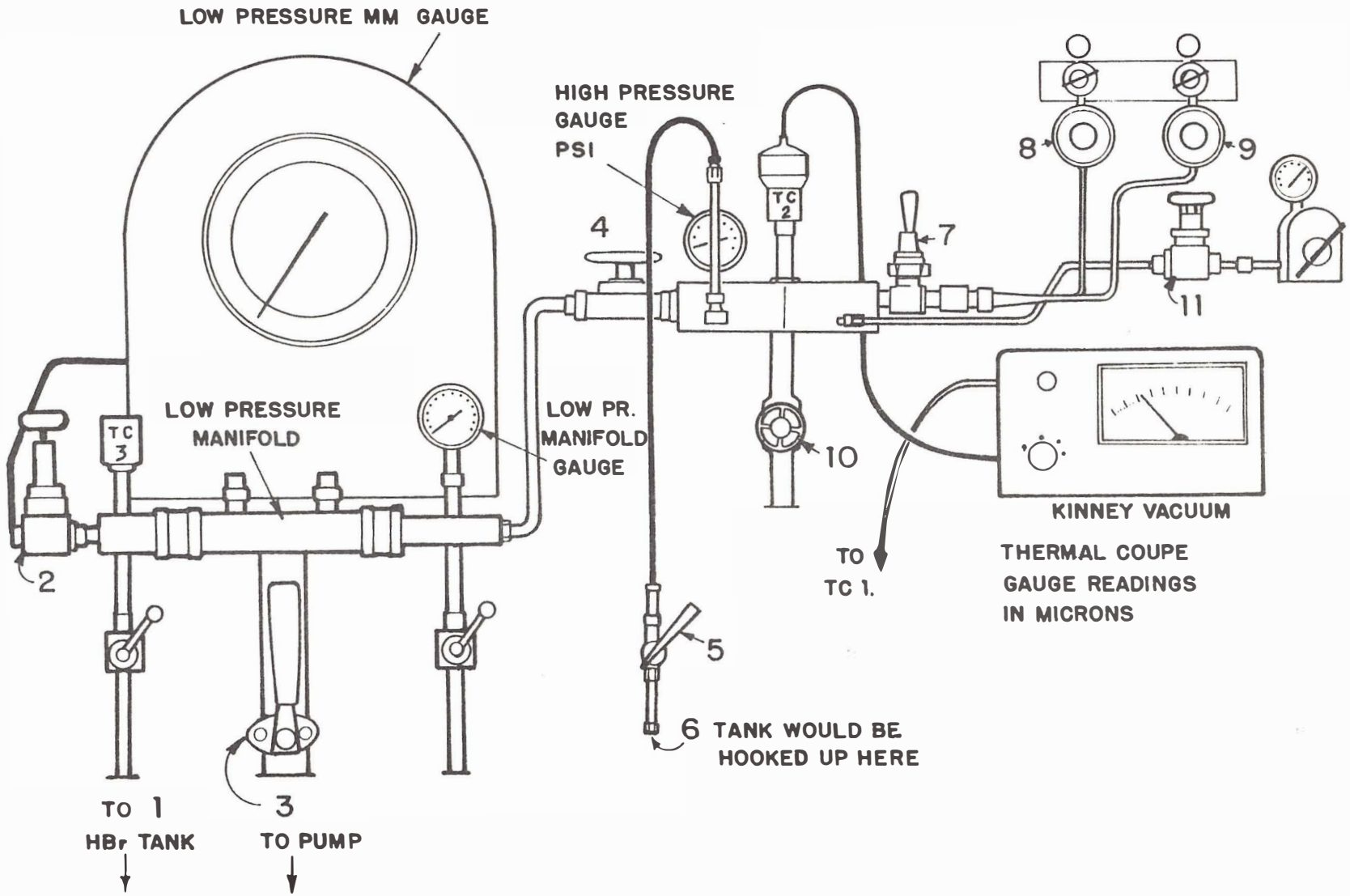
9. N_2 (fill gas line valve)

#10. H.P.vac (high pressure shut off to vacuum pump valve)

#11. External gas (Kr or tank of external gas valve)

CAUTION: MAKE SURE HIGH PRESSURE DOES NOT GET THROUGH TO LOW PRESSURE SIDE EITHER THROUGH #4 OR THROUGH PUMP AND #3 VALVE.

MIXING HYDROGEN BROMIDE [ONLY] IN CARRIER GAS FOR LAMP FILL



PREPARATION OF HALOGEN DOSED FILL GAS

The fill gas tanks can be made in several sizes and filled to various pressures. The highest pressure is usually 10 atmospheres. The bigger the tank and the higher the pressure, the more lamps can be made without changing tanks. However, since the halogen dose is mixed with the fill gas not chemically combined, stratification is more likely to occur in large tanks. For this reason production tanks usually vary from 5 to 100 liter size. The tanks are usually made of monel because of the resistance of monel to attack by all halogens.

The mixing is done by partial pressure. For example, if a 0.50% mixture of HBr and nitrogen was specified and the tank pressure was to be 10 atmospheres, the partial pressue of HBr would be calculated as follows:

HBr partial Pressure = 0.5% of 10 Atmosphere

= .005 X 10 X 760 Torr

= 38. Torr

An evacuated tank would be filled with HBr to a pressure of 38 Torr. Nitrogen would then be added to make up a total pressure of 10 atmospheres (7600 Torr) or (10 Bars) or 10 x 10^5 Pa).

11.1 BROMINE CARRIER GAS IDENTIFICATION NUMBER SYSTEM

The inert fill gas is usually identified by a code. The GTE code is as follows:

A	-	Argon
N	-	Nitrogen
K	-	Krypton
AN7030	-	Argon 70% Nitrogen 30%
AN8812	-	Argon 88% Nitrogen 12%
AN955	-	Argon 95% Nitrogen 5%
ANO	-	Argon 88% Nitrogen 11.9% Oxygen 0.01%
KN5050	-	Krypton 50% Nitrogen 50%
KN7030	-	Krypton 70% Nitrogen 30%
KN8812	-	Krypton 88% Nitrogen 12%
KN955	-	Krypton 95% Nigrogen 5%

% HBR	100% N_2	100% Ar	100% Kr	Argon with Nitrogen -(N_2%) 5%	Argon with Nitrogen -(N_2%) 12%	Argon with Nitrogen -(N_2%) 30%	Argon with 12% Nitrogen .01% Oxygen	Krypton with Nitrogen -(N_2%) 5%	Krypton with Nitrogen -(N_2%) 12%	Krypton with Nitrogen -(N_2%) 30%	Krypton with Nitrogen -(N_2%) 50%
0.097	N1	A1	K1	AN57	AN29	AN1	ANO-1	KN85	KN57	KN29	KN1
0.15	N2	A2	K2	AN58	AN30	AN2	ANO-2	KN86	KN58	KN30	KN2
0.19	N3	A3	K3	AN59	AN31	AN3	ANO-3	KN87	KN59	KN31	KN3
0.24	N4	A4	K4	AN60	AN32	AN4	ANO-4	KN88	KN60	KN32	KN4
0.29	N5	A5	K5	AN61	AN33	AN5	ANO-5	KN89	KN61	KN33	KN5
0.39	N6	A6	K6	AN62	AN34	AN6	ANO-6	KN90	KN62	KN34	KN6
0.41	N7	A7	K7	AN63	AN35	AN7	ANO-7	KN91	KN63	KN35	KN7
0.44	N8	A8	K8	AN64	AN36	AN8	ANO-8	KN92	KN64	KN36	KN8
0.49	N9	A9	K9	AN65	AN37	AN9	ANO-9	KN93	KN65	KN37	KN9
0.61	N10	A10	K10	AN66	AN38	AN10	ANO-10	KN94	KN66	KN38	KN10
0.73	N11	A11	K11	AN67	AN39	AN11	ANO-11	KN95	KN67	KN39	KN11
0.78	K12	A12	K12	AN68	AN40	AN12	ANO-12	KN96	KN68	KN40	KN12
0.91	N13	A13	K13	AN69	AN41	AN13	ANO-13	KN97	KN69	KN41	KN13
0.97	N14	A14	K14	AN70	AN42	AN14	ANO-14	KN98	KN70	KN42	KN14
1.2	N15	A15	K15	AN71	AN43	AN15	ANO-15	KN99	KN71	KN43	KN15
1.5	N16	A16	K16	AN72	AN44	AN16	ANO-16	KN100	KN72	KN44	KN16
1.7	N17	A17	K17	AN73	AN45	AN17	ANO-17	KN101	KN73	KN45	KN17
1.8	N18	A18	K18	AN74	AN46	AN18	ANO-18	KN102	KN74	KN46	KN18
1.9	N19	A19	K19	AN75	AN47	AN19	ANO-19	KN103	KN75	KN47	KN18
2.1	N20	A20	K20	AN76	AN48	AN20	ANO-20	KN104	KN76	KN48	KN18
2.2	N21	A21	K21	AN77	AN49	AN21	ANO-21	KN105	KN77	KN49	KN21
2.4	N22	A22	K22	AN78	AN50	AN22	ANO-22	KN106	KN78	KN50	KN22
3.0	N23	A23	K23	AN79	AN51	AN23	ANO-22	KN107	KN79	KN51	KN23
3.6	N24	A24	K24	AN80	AN52	AN24	ANO-23	KN108	KN80	KN52	KN24
4.2	N25	A25	K25	AN81	AN53	AN25	ANO-24	KN109	KN81	KN53	KN25
4.8	N26	A26	K26	AN82	AN54	AN26	ANO-25	KN110	KN82	KN54	KN26
6.1	N27	A27	K27	AN83	AN55	AN27	ANO-26	KN111	KN83	KN55	KN27
7.3	N28	A28	K28	AN84	AN56	AN28	ANO-27	KN112	KN84	KN56	KN28

NOTES:
1. See 10B0707-0048 and 10B0707-0050 for mixing instructions
2. See 5750-XXXX assembly series for additional combinations and details.

BROMINE - CARRIER GAS IDENTIFICATION

12.0 SOURCES OF CONTAMINATION IN HALOGEN LAMPS

The halogen cycle is sensitive to several impurities that can be found in lamps unless they are specially processed. Sources of impurities include:

A. The Filament
B. Leads
C. Supports
D. Bulb
E. Weld Flux
F. Fill Gas
G. Halogen Dose Composition

The filament, leads and supports have been identified to be the major source of contamination in quartz halogen lamps. In quartz lamps, the leads, supports and filament are all lamp wire tungsten.

Observations indicate the liberation from the coil of a variety of atomic species during incandescence. These atoms come from impurities originally present in the ore, which are not removed during the preparation of tungsten, or from impurities introduced during the processing of the filament; or they originate from the doping of the material. The liberation of atoms from the coil during incandescence can also be traced by activation analysis of the coil material before and after a burning period. The spectroscopic results clearly establish that different spectral patterns originate from filaments of different origins. The results further indicate the important influence of differences in the reactive transport gases.

Consequently the following three types of processes must be considered.

(i) Evaporation during the whole duration of incandescence; This will be the case for the atoms W and Mo.

(ii) Evaporation of atoms during short periods, e.g., at the beginning of incandescence: The steady state of excited atoms in the hot zone around and within the filament is maintained by some kind of transport reaction primarily due to the presence of the reactive gas. Presumably the atoms involved are Fe, V

and Ti. In this case the impurity atoms interfere with the tungsten halogen cycle. This process may have important consequences for lamp behavior at low halogen concentrations.

Chemical reactions due to the transport gas:
The observation of the atoms Al, Cr and perhaps also Ti is attributed to the presence of carbon. These metals are present as oxides. The following mechanism is suggested: at low temperatures (∿500°C) the initially present CH_2Br_2 is pyrolyzed. The resulting carbon precipitates onto the filament and subsequent reduction of oxides at high temperatures take place.

The presence of potassium in the gas phase could not be detected (using the resonance line at 766 nm). However, K comes out of the filament by heating in vacuum, as is well known from mass spectroscopy.

12.1 BULB

The bulb is a source of impurities. The actual impurities and the quartz vary with the bulb composition.

Figure 12.1.1 is a table of bulb glasses for quartz and hard glass halogen lamps.

12.1.2 QUARTZ

Quartz is also known as Vitreous Silica, Silica Glass, and Fused Silica is essentially Silicon Dioxide SiO_2. The purity of the lamp quartz is related to the purity of the quartz crystal raw material.

This crystal is graded to some extent at the mines and the manufacturers, themselves, examine the material for surface contamination, "twinning" and "ghosting" (optical defects which can be co-related to some extent with chemical purity), and for inclusions in the crystal. In spite of such examinations, which cannot of course detect impurities present as substitutioned ions and interstitial ions in the silica lattice but only

macro-defects, there may still be a large variation in the amount present of a particular impurity not only from one batch of crystal to the next, but even within one batch of crystal and conceivably within a single length of tubing made from crystal. It must be emphasized that these variations mentioned are referred to very low impurity levels!

Thus it is difficult for a manufacturer to give a guaranteed or even a typical analysis for any one grade of vitreous silica made from quartz minerals.

The above remarks apply to material made by fusing quartz crystal. They do not apply to synthetic vitreous silicas where the impurity levels are much lower and are not subject to the same raw material variations as in crystal, being made from a readily purifiable, volatile silicon compound. The impurity levels present in these materials can therefore be given more confidently although it can be seen from Table 1 that, because only very small amounts of impurity are present, they are usually beyond the levels of detection of present routine analytical methods.

Metallic impurities present in vitreous silica are, with the exception of alkali and alkaline earth cations, usually not present as ions but are incorporated in the silica network, generally occupying a position normally occupied by a silicon atom. These impurity atoms are therefore very firmly bound and are not released in high temperature work unless the vitreous silica is dissolved or volatilized.

Figure 12.1.1

BULB GLASSES FOR HALOGEN LAMPS

	QUARTZ	VYCOR	GE 177	GE 180	1766	1720	1723	7725
SOFTENING POINT	1670	1530	1130	1020	944	915	910	770
ANNEAL POINT	1140	1020	865	805	749	712	710	550
STRAIN POINT	1070	890	805	755	705	667	670	515
EXPANSION	5.5	7.5	38	43	52.5	42	46	38
ELEC. RES. 250°	11.8	9.7	12.2	12.7	15.9	10.8	12.5	
ELEC. RES. 350°	10.2	8.1	10.5	11.1	13.0	9.0	11.3	

TABLE 1
Chemical Purities of Vitreous Silica

(Maximum levels so far determined in ppm)

Element	Translucent Vitreous Silica	Transparent Vitreous Silica*		
		Type I	Type II	Type III†
Aluminum	380	70	60	<0.02
Antimony	ND	0.3	0.1	<0.0001
Boron	7	3	3	<0.01
Calcium	10	0.5	0.4	<0.1
Copper	ND	1	1	0.002
Iron	70	2	1.5	<0.1
Manganese	ND	0.03	0.02	<0.001
Phosphorous	ND	0.01	0.005	<0.001
Sodium	60	4	1	0.04

ND = Not determined
* The types referred to are those described in the text.
† Analyses made on ingot material.
(The metallic impurities in Type IV vitreous silica are similar to those in Type III material.)

Type I transparent vitreous silica is usually obtained by electric melting quartz crystal powder in vacuum or in an inert gas at low pressure. It contains negligible "water" but about the same metallic impurities as the unfused raw material (e.g., I.R. Vitreosil).

One type of fused quartz tubing is made by a continuous process, the quartz crystal being melted in a refractory metal pot at atmospheric pressure and the tubing drawn from the bottom of the pot through a die (Hanlein process). This tubing suffers the disadvantage of long air lines and the "water" content is somewhat higher than other Type I materials, resulting from the protective atmosphere enveloping the furnace.

Type II is prepared by fusion of quartz crystal in a flame, and like all vitreous silicas prepared in a water vapor atmosphere it contains varying concentration of hydroxyl (usually 0.015-0.04 wt % OH) depending on the fusing conditions and the size of the quartz crystal particles

used. Some impurities (e.g. aluminum) may be partially volatised in the flame giving, generally, lower maximum impurity levels for this type (Vitreosil 066).

Type III "synthetic" vitreous silica is made by the vapor-phase hydrolysis of a pure silicon compound such as silicon tetrachloride and simultaneous fusing of the silica formed in for example, an oxy-hydrogen flame. It has the highest hydroxyl content (about 0.1 wt. % OH) but is virtually free from metallic impurities (e.g., total metallic contamination in Spectrosil 0.2 ppm). When made from silicon tetrachloride the material contains about 50 ppm chlorine.

12.1.3 VYCOR

Vycor (a trade-marked hybrid 96% silica material manufactured by Corning Glass Works) is intermediate in temperature tolerance between quartz and the conventional hard glasses and is currently used in certain applications for many tungsten-halogen lamps.

Vycor is a reconstructed glass, the outgassing characteristics can be engineered by degassing the glass prior to and during consolidating the pores.

This is illustrated in Figure 6 , which compares the outgassing behavior of Code 7900 glass aginst Code 7911 glass.

The material that is outgassed from Vycor is mostly water vapor.

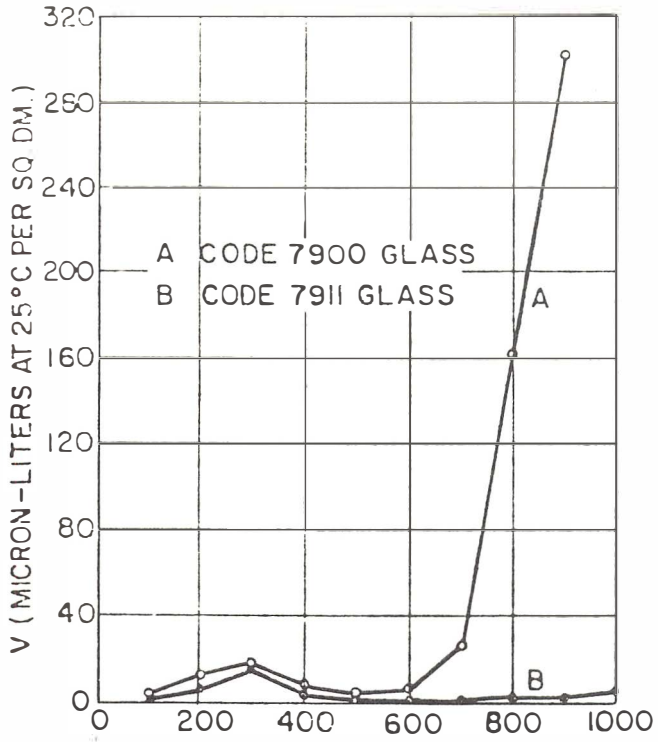


Figure 6

Outgassing curves for two VYCOR Brand high silica glasses. See Section

12.1.4 HARD GLASS

The hard glasses for halogen lamps are in two types:

A. Borosilicate Glasses

Typical	Composition is:
SiO_2	75.5%
Al_2O_3	2.6%
Na_2O	3.7%
K_2O	1.7%
B_2O_3	16.0%

These glasses include:

Corning #7740
#7720
#7725

B. Aluminositicate Glasses

Typical Composition is:

SiO_2	51.2%
Al_2O_3	22.6%
CaO	9.0%
MgO	5.4%
BaO	5.3%
B_2O_3	1.5%
P_2O_5	4.5%

These glasses include:

Corning	#1720
	#1776
	#1723
G.E.	# 177
	# 180
Osram	# 943

The materials which can evolve from these glasses include water vapor, carbon monoxide, carbon dioxide, hydrogen, sodium, potassium and other alkali materials. Water vapor, CO and CO_2 are halogen cycle accelerators, the alkali materials and hydrogen tend to slow the halogen reaction rate by tying up available halogen.

Water vapor is by far the greatest impurity which evolves from the bulb. Figure 7 shows the rate of water vapor release increases with temperature and decreases from borosilicate glass to aluminosilicate glass to Vycor and quartz.

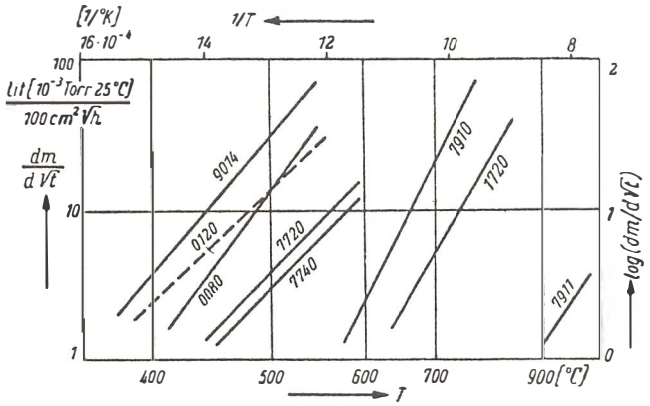


Figure 7

"Rate" of Water Vapor Release $dm/d(\sqrt{t})$ as a Function of Temperature T(°C) and of 1/T(1/K) for a Series of Commercial Glasses made by Corning (Todd)

12.2 GLASS TO METAL SEALS AND LEADS

12.2.1 MOLYBDENUM

Moly is used as a lead material in hard glass halogen lamps. Moly is not generally used inside of quartz lamps.

In hard glass lamps, where the lead in material is moly wire, a considerable range of temperature is experienced by the moly leads. The coolest point is at junction of glass and hottest at point where filament enters the moly clamp. If the temperatures are high enough, moly can be transferred by same reactions as the tungsten halogen cycle. In fact, moly leads react with bromine and any oxygen present faster than tungsten leads.

Untreated moly lead wire has a much higher impurity level than etched moly wire.

Table 2 shows the results of optical emission spectrograph analysis of as drawn and etched GE type Kw moly wire.

TABLE 2

IMPURITY LEVELS PPM

	As Drawn Wire				Caustic Etched Wire			
	.012" dia.		.020" dia.		.012" dia.		.020" dia.	
	Surface	Core	Surface	Core	Surface	Core	Surface	Core
Fe	80	43	80	39	50	41	61	43
Cr	23	18	24	17	18	14	20	17
Ni	13	8	10	9	10	7	11	8
Ca	13	13	13	13	13	13	13	13
Cu	4	4	5	4	5	4	10	5
Mn	14	16	17	17	18	15	19	16
Mg	10	10	12	10	12	11	16	10
Sn	16	23	15	22	15	22	20	27
Co	8	8	8	8	8	8	8	8
Ti	10	10	10	10	10	10	10	10
Pb	10	10	10	10	10	10	10	10
Zr	10	10	10	10	10	10	10	10

12.3 TUNGSTEN TO MOLY WELD

The most common method of attaching the legs of a halogen lamp filament to the moly sealing ribbon is by welding. Since moly to tungsten is a difficult weld, it is common to use platinum as an intermediate. In other words, the moly is welded to Pt which is also welded to the tungsten. The Pt is used as a piece of wire, ribbon or sometimes plated on the moly ribbon on one side.

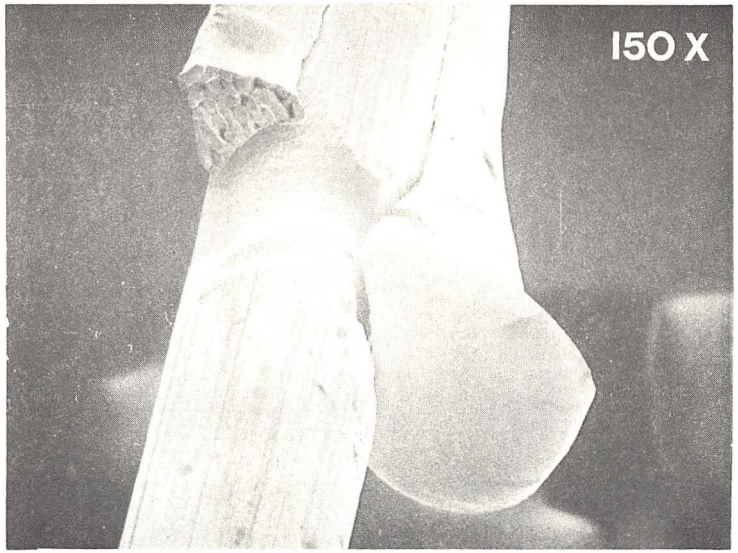
Any Platinum that is seen by the halogen acts as a contact catalyst and speeds up the rate of attack of halogen on the cooler parts of the lamp. In some lamps, where Pt wire and/or ribbon is used, there is excess Pt which softens and extrudes up the lead when the quartz press real is made. This can cause lead failure 10 times faster than

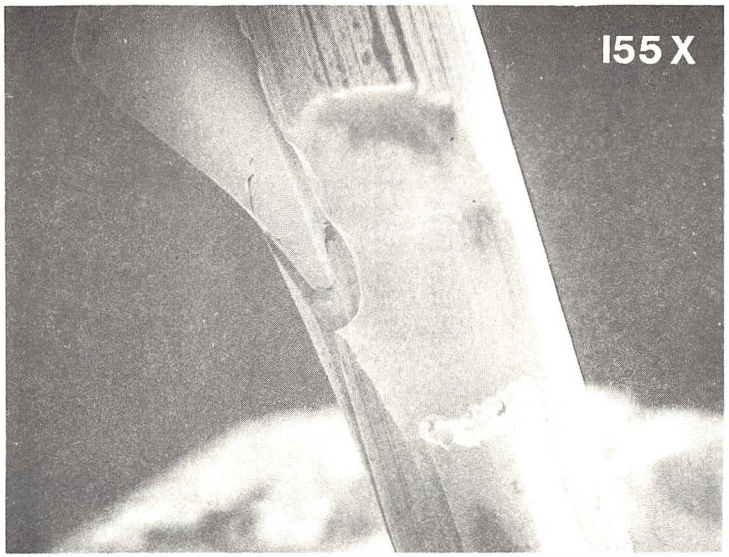
than when no Pt is present. The following SEM pictures of 1500W/120V Linear Lamps show the effect. The glass from the press was removed to take the pictures. The attack is mostly at junction of press, but also down into the press.

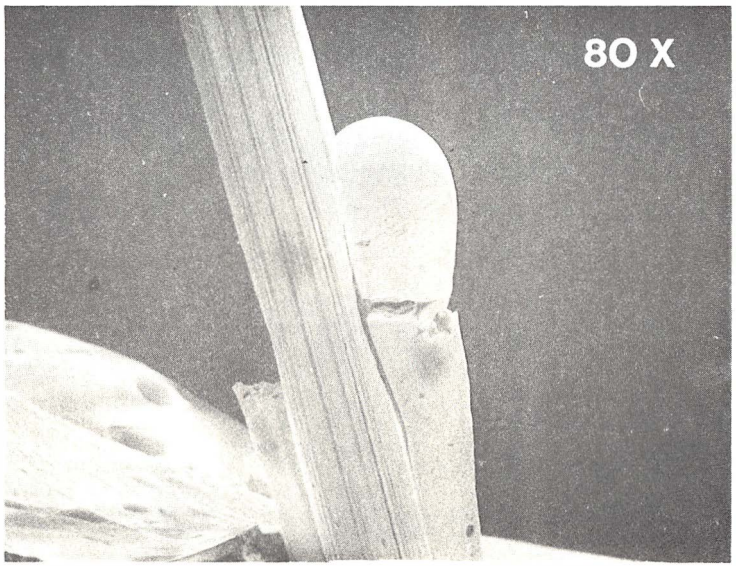
The fact that the bromine enters the press was proved by making some lamps wherein the Pt was replaced by Ta. Over a period of a few hundred hours, the Ta disappeared. It was converted to a gaseous Ta halide.

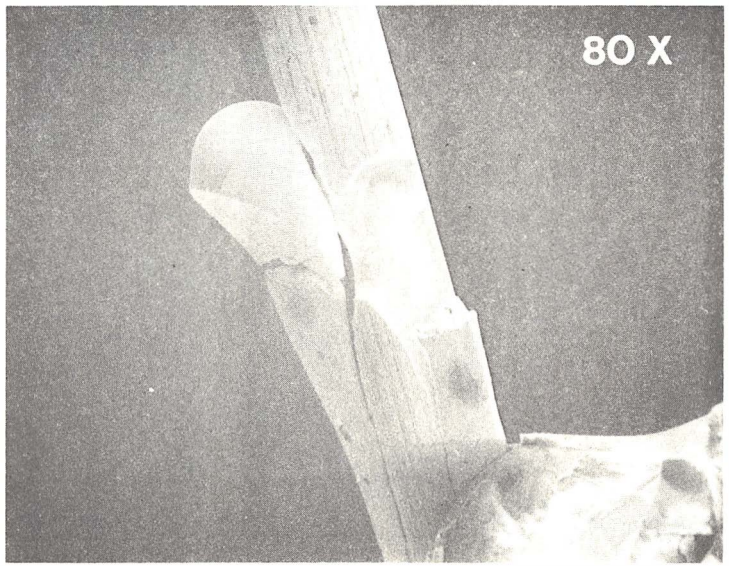
1500W/240V QUARTZ HALOGEN LAMP

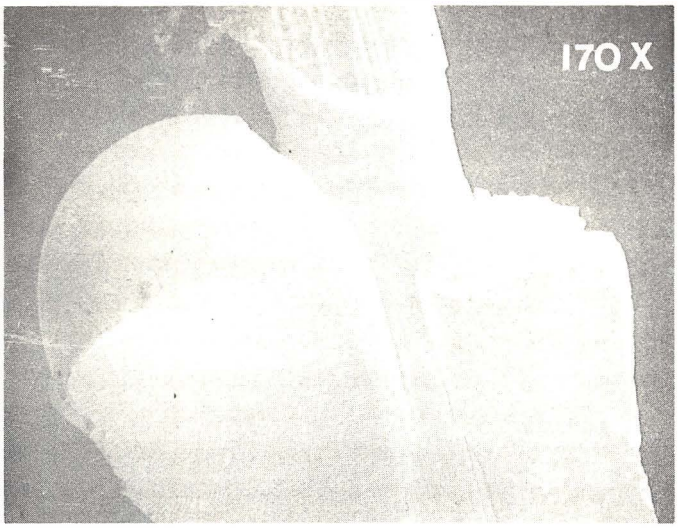
Platinum/Tungsten Interaction Area - Sample 1

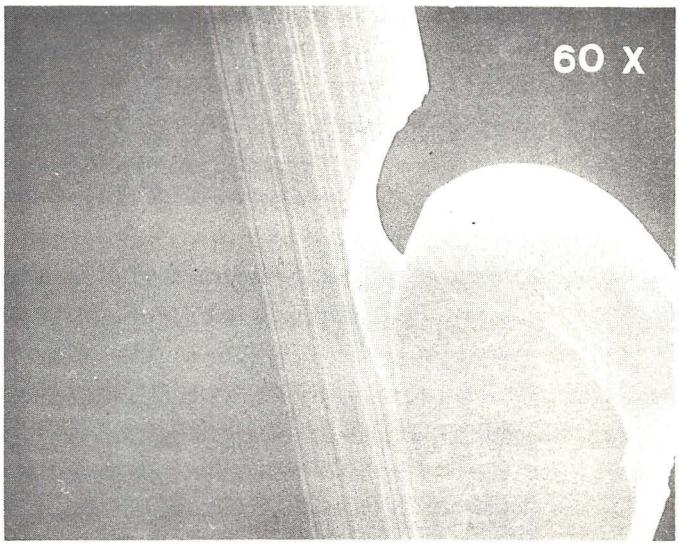


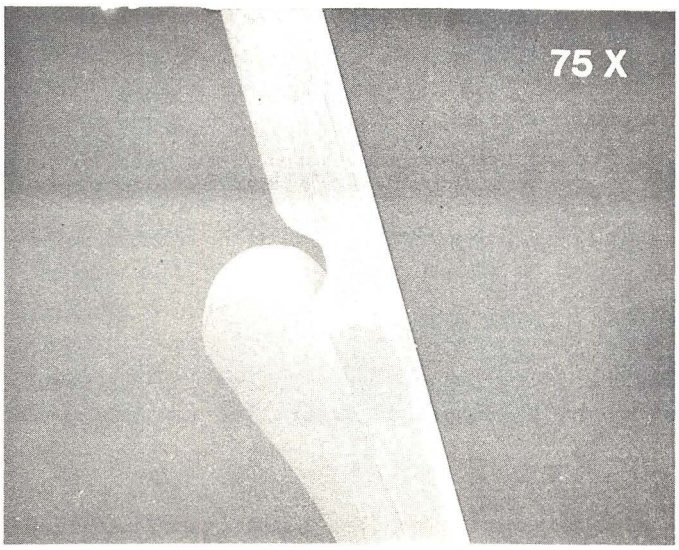






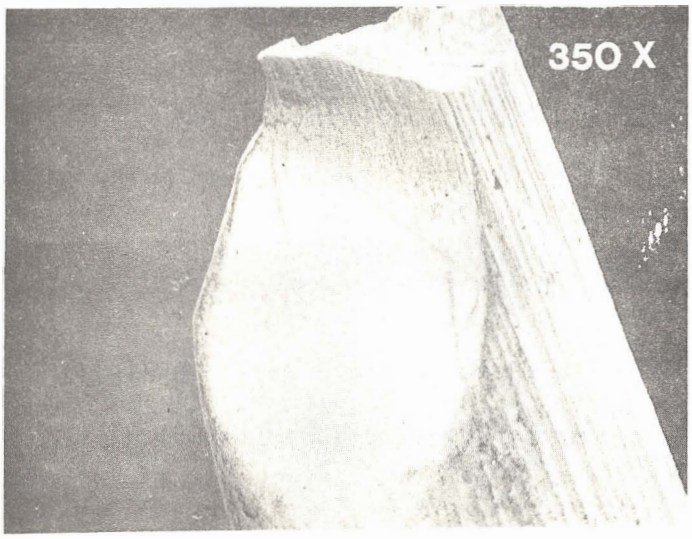


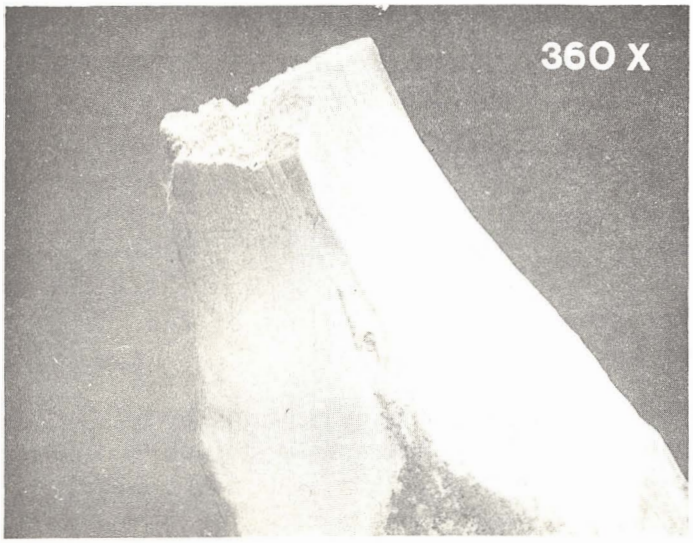


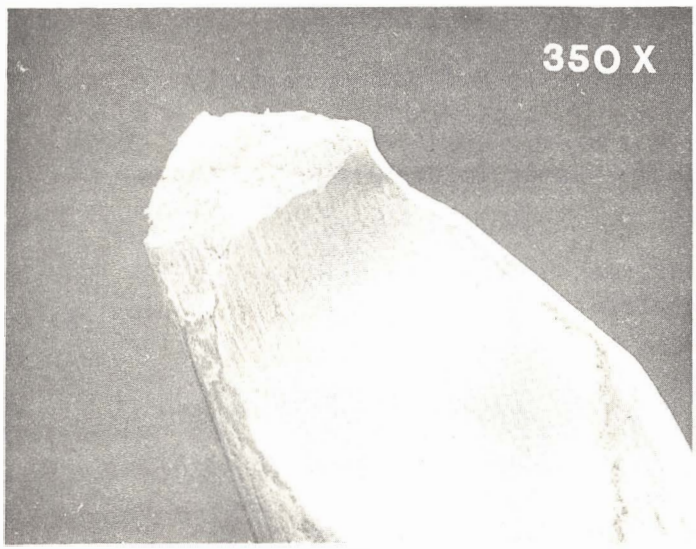


1500 W/240 V
QUARTZ HALOGEN

Platinum/Tungsten
Interaction Area
Sample 2







1500W/240 V
QUARTZ HALOGEN

Tungsten
Wire from Lamp
at Failure Point

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13.0 HALOGEN LAMP CONSTRUCTION MATERIALS

13.1 Glasses for Tungsten-Halogen Lamps

Tungsten-halogen lamps are incandescent gas-filled lamps with a halogen added to the gas filling. Under suitable conditions some of the tungsten which evaporates from the filament and diffuses towards the lamp envelope combines with the halogen and is transported back towards the filament. The tungsten and the halogen dissociate at the higher temperature, the tungsten being deposited on the filament and the halogen being available to continue the reaction cycle.

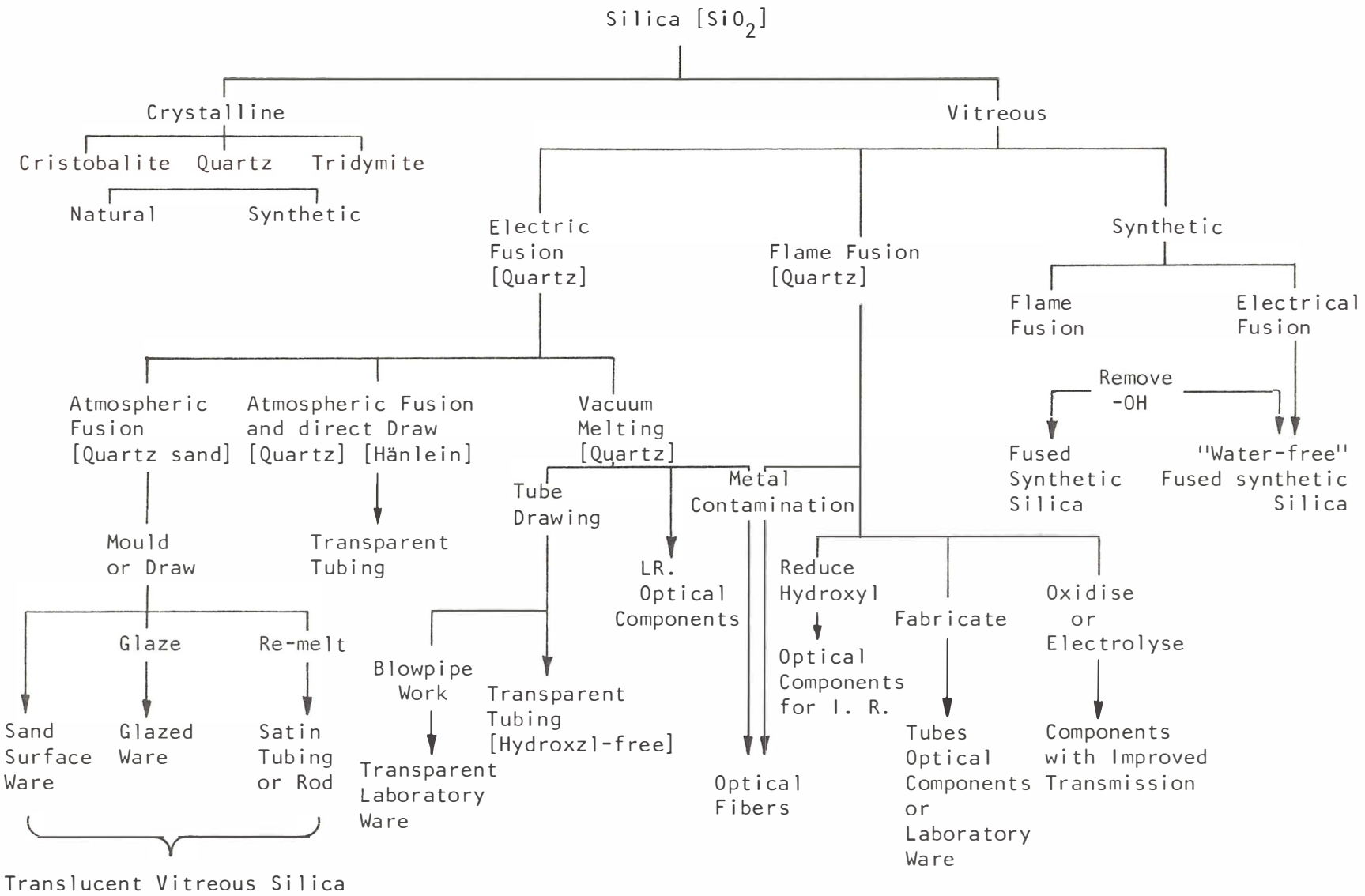
Iodine was the halogen used in the first commercial lamps. It was established that a minimum envelope temperature of 700°C and elimination of all traces of water vapor from within the lamps were essential to ensure satisfactory operation of the tungsten-iodine cycle. As conventional almuninosilicate and borosilicate glasses continue to evolve water vapor at these temperatures, even after thorough processing, it is necessary to use vitreous silica for the envelopes of high bulb temperature lamps especially iodine lamps.

Not all types of vitreous silica are suitable for such applications as some types will evolve hydrogen or water vapor, for example, under the conditions of lamp manufacture or operation. The behavior of any type of vitreous silica depends largely on its method of manufacture and its thermal history.

The use of bromine compounds in place of iodine allowed greater freedom in envelope design, as the tungsten-bromine cycle will operate satisfactorily with envelope temperatures in the range 200-1100°C. Moreover the effect of the presence of water vapor is much less significant so that for some lamps an envelope incorporating aluminosilicate and borosilicate glasses can be used.

The choice between vitreous silica and other glasses must be considered carefully for each design of lamp, its rating and designed life and its application. The majority of tungsten-halogen lamps have vitreous silica envelopes although for some types a 96% silica glass is used. A limited number have aluminosilicate or borosilicate glass envelopes.

Table 1 FORMS OF CRYSTALLINE AND VITREOUS SILICA



QUARTZ

Quartz is often referred to as vitreous silica, fused silica, quartz glass, fused quartz or simply quartz.

Quartz is chemically defined as silicon dioxide, SiO_2 and is a common substance found in nature.

The most common form of silica from the point of view of a glassblower is, of course, vitreous silica; therefore the terminology used, and the material itself, will now be considered in more detail.

Opaque or translucent vitreous silica, the form commonly obtained by the fusion of sand and which derives its translucency from the minute gas bubbles disseminated in the structure, is commonly referred to as "fused silica." Transparent vitreous silica, usually made by the fusion of quartz crystal, is referred to as "fused quartz" or sometimes "quartz glass."

Vitreous silica can thus be subdivided into two major groups; translucent vitreous silica, which is made by the fusion of quartz sand in a furnace open to the atmosphere, and transparent vitreous silica, which, until a few years ago, was always made by the fusion of quartz crystal, but which now can be made also by the hydrolysis or oxidation of a volatile silicon compound and the subsequent fusion of the silica so formed.

These two major groups can be subdivided further as follows:

Translucent Vitreous Silica

Sand surface ware is the quality obtained directly by the electrical fusion of pure silica sand, the unfused sand adhereing to the outer surface after fusing and moulding usually being removed by abrasion.

Glazed ware is a modification of the sand surface product obtained by remelting the surface, and often reshaping the article, in a flame or electric arc. The material is homogeneous throughout, no fluxes being added.

Satin tubing or rod is made by heating externally a fused mass of sand during the drawing operation; the striated bubbles giving the tubine or rod its characteristic sheen.

Transparent Vitreous Silica

It is not intended here to give a detailed discussion on the methods of making transparent vitreous silicas but four fundamentally different types can be recognized with diferences based principally on methods of fusing and on "water" and metal impurity concentrations.

Type I transparent vitreous silica is usually obtained by electric melting quartz crystal powder in vacuum or in an inert gas at low pressure. It contains negligible "water" but about the same metallic impurities as the unfused raw material.

One type of fused quartz tubing is made by a continuous process, the quartz crystal being melted in a refractory metal pot at atmospheric pressure and the tubing drawn from the bottom of the pot through a die (Hanlein process). This tubing suffers the disadvantage of long air-lines and the "water" content is somewhat higher than other Type I materials, resulting from the protective atmosphere enveloping the furnace.

Type II is prepared by fusion of quartz crystal in a flame, and like all vitreous silicas prepared in a water vapor atmosphere it contains varying concentrations of hydroxyl (usually 0.015-0.04 wt. %OH) depending on the fusing conditions and the size of the quartz crystal particles used. Some impurities (e.g. aluminum) may be partially volatilized in the flame giving, generally, lower maximum impurity levels for this type (e.g., Vitreosil 066).

The flame fusion method has some advantages over electrical methods where thick sections are being made in that, since the vitreous material is deposited in thin layers, bubbles are less likely to be trapped in the material and, secondly, it is easier to fuse the material completely to obtain a random structure and hence a material which appears more "glassy." However, the "water" included in the silica structure is linked to the silicon-atoms as Si-OH groups, breaking up the tetrahedra. This has a noticeable effect on such physical properties as the infra-red transmission, viscosity and density. Subsequent flame-working of electrically fused material also introduces "water" to give Si-OH linkages.

It has already been indicated that heating vitreous silica in a water-vapor atmosphere (e.g., a flame) introduces hydroxyl. Conversely, it is possible to reduce the material's hydroxyl content by subjecting the vitreous silica to an appropriate heat treatment in a dry, hydrogen-free atmosphere.

During or subsequent to the fusion process, small amounts of metal (e.g., tin, manganese, titanium) or their oxides can be used to contaminate the vitreous silica and so produce materials which, although behaving as vitreous silica in their mechanical and thermal properties, have modified optical transmission properties which are sometimes useful. One obvious example is that of producing a vitreous silica envelope for mercury vapor lamps which filters out the ozone-producing radiation.

It is now obvious that instead of simply "vitreous silica" there are a number of materials, all essentially vitreous silica, but varying in the randomness of their structure (from fused quartz which, because of the similarity in the structures of the crystalline and vitreous phases and the high viscosity of the melt, must contain some residual crystal structure, to the completely random synthetic vitreous silicas which have no crystal origin), in their freedom from physical defects such as bubbles, in their chemical purity and in particular, in their hydroxyl contents.

With this in mind, it is now possible to examine the effect these differences have on the properties of vitreous silica of most interest to glassblowers and lamp designers.

PURITY

Almost all commercial grades of vitreous silica are "pure" in the sense that even for the translucent material the total maximum metallix impurity levels are only about 1,000 ppm (0.1 wt. %) and in the transparent grades perhaps 150 ppm (0.015 wt. %). Thus, particularly in the case of transparent vitreous silica, analysis is difficult, expensive and not always sufficiently accurate for someone only interested in a particular impurity. Another important factor to be borne in mind is variability in the impurity levels. Most manufacturers of transparent vitreous silica obtain their quartz crystal from Brazil but there is still a considerable variation in the purity of their raw material.

Thus it is difficult for a manufacturer to give a guaranteed or even a typical analysis for any one grade of vitreous silica made from quartz minerals.

One is of course able to give the maximum values of an impurity so far determined, but since generally these values are much higher than in the majority of specimens, they should not be compared with "typical" values or those resulting from a single analysis.

CHEMICAL PURITIES OF VITREOUS SILICA

(Maximum levels so far determined in ppm)

	Translucent Vitreous Silica	Transparent Vitreous Silica*	
		Type I	Type II
Aluminum	380	70	60
Antimony	ND	0.3	0.1
Boron	7	3	3
Calcium	10	0.5	0.4
Copper	ND	1	1
Iron	70	2	1.5
Manganese	ND	0.03	0.02
Phosphorous	ND	0.01	0.005
Sodium	60	4	1

ND = Not determined

* The types referred to are those described in the text.

Metallic impurities present in vitreous silica are, with the exception of alkali and alkaline earth cations, usually not present as ions but are incorporated in the silica network, generally occupying a position normally occupied by a silicon atom. These impurity atoms are therefore very firmly bound and are not released in high temperature work unless the vitreous silica is dissolved or volatilized.

The impurities so far referred to, stem largely from the original raw material employed. Manufacturing processes and fabrication are also sources of contamination, and while manufacturers take all possible precautions in this respect it is worthwhile mentioning contamination which can occur in

the handling of these materials. Copper is a common contaminant since it occurs in the nozzles of normal blowpipes and in many bonded diamond cutting wheels. Moreover, it has a high "diffusion coefficient," which means that if introduced on to a surface it will rapidly diffuse into the material. Thus, while surface contamination from blowpipes and cutting wheels might be expected to be removed subsequently by etching the surface with hydrofluoric acid, it may not always be possible to remove contamination such as copper in this way.

It is necessary to add that vitreous silica should be scrupulously clean before being subjected to high temperatures which will cause reaction with metallic impurities occurring in dust, fingerprints or tap water.

It is not usually possible to judge the chemical purity of vitreous silica by a visual examination, except for obvious inclusion spots which may have characteristic colors (e.g, iron-black; titanium-blue; copper-red). Some information can however be obtained by observing the color of the fluorescence emitted when the article is irradiated by ultra-violet light (e.g., from a low pressure mercury vapor lamp.) Under these conditions a green color generally indicates copper although this may be masked sometimes by the blue-violet fluorescence normally associated with fused crystal quartz and caused by metals, such as aluminum, in a reduced state. It is difficult to estimate, even semi-quantitatively, the level of contamination from a visual examination of the emitted fluorescence, as the sensitivity of the human eye varies markedly with the color observed.

The reaction of water with silica is a reversible equilibrium process and may be represented by the equation:

$$\text{Si-O-Si} + H_2O \rightleftharpoons \text{Si-OH} + \text{HO-Si}$$

indicating that the hydroxyl content of vitreous silica is not a fixed amount but can vary continuously (although usually slowly) with changing conditions. Given time to establish equilibrium, the hydroxyl content depends on the amount of water in the atmosphere surrounding the piece of vitreous silica and is, in fact, proportional to the square root of the partial pressure of water vapor in the atmosphere at a particular temperature.

From the lampmaker's point of view, no vitreous silica can be regarded as completely "water-free" if it has had any blowpipe treatment since blowpipe flames contain large amounts of water vapor, as a product of combustion. In this respect oxy-hydrogen flames introduce hydroxyl more quickly into vitreous silica than do oxy-propane flames.

THERMAL PROPERTIES

The low expansion of vitreous silica makes it unique among high temperature materials in its resistance to thermal shock.

	Fused Quartz
Softening Point (°C)	1670
Anneal Point (°C)	1140
Strain Point (°C)	1070
Expansion (0-300°C)X 10^{-7}cm/cm/°C	5.5
Density	2.20

Devitrification

Vitreous silica is an unstable form but at temperatures below 1,050°C it will remain in this form regardless of temperature changes. Above 1,050°C there is a slow and irreversible change to B-cristobalite. Under clean conditions this process occurs slowly and is a surface effect. This white devitrification will often have been observed on vitreous silica subjected to temperatures above 1,050°C, but it should not be confused with the white deposits of evaporated silica left after quartz pressing or forming.

This B-cristobalite does not initially harm a vitreous silica component as its coefficient of thermal expansion is quite close to that of the vitreous material. However, as the temperature falls the B-cristobalite changes to a-quartz via B-quartz at 570°C or to a-cristobalite at about 270°C. These phase changes are accompanied by large volume changes and consequently the materials are not compatible with the low expansion vitreous silica substrate and will flake off. If, on the other hand, a considerable part of the vitreous silica has been devitrified the strength of the crystalline material will be greater than the remaining vitreous silica and the component will shatter.

Devitrification is a "nucleation" process, that is it spreads from centres of impurity or mechanical surface imperfections. For this reason it is usually worthwhile to fire polish a surface which has been treated in hydrofluoric acid so as to restore a "glassy" surface.

Although components may be heated for hundreds of hours at temperatures above 1,050°C under very clean conditions, very small amounts of contamination by alkali ions (sodium, potassium, lithium, calcium, etc.) will accelerate devitrification. Even fingermarks or tap-water stains will produce the effect very quickly and scrupulous cleanliness is vital in preparing components for blowpiping or high temperature work.

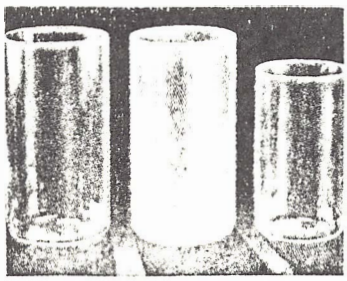
13.1.2 VYCOR

Vycor is the Corning trade name for a high SiO_2 content (95% or more) glass. The glass is made by a four-step process.

1. The starting material is a base glass whose composition is approximately 75% SiO_2, 20% B_2O_3 and 5% alkali oxides. This glass can be processed like any ordinary hard glass. Tubing can be drawn, bulbs blown, etc.

2. The basic glass article now undergoes about a 5 hour treatment at 600 - 650°C. The glass components separate into two non-crystalline, glassy phases. One phase is alsmot solely B_2O_3 and alkali oxides. The other is predominantly a porous, but coherent silica-sponge skeleton.

3. After leaching, the SiO_2 skeleton is sintered at 900 - 1000°C. The porous skeleton shrinks in all directions by about 14% to form a pore free, fully-glass body made of 95+% fused quartz.



I II III

Manufacturing Process for Vycor ware, from 95-96% SiO_2.

I blown basic glass
II the same piece after dehomogenizing and acid-leaching
III the same after sintering at about 1000°
(Corning)

The working of Vycor is very similar to that of true quartz.

If the highest possible UV transmission (lowest H_2O content) is desired, extra steps during the sintering process are required.

The termal properties of Vycor are similar to quartz.

	QUARTZ	VYCOR
Softening Point	1670	1530
Anneal Point	1140	1020
Strain Point	1070	890
Expansion	5.5	7.5
Elec Res. 250°C	11.8	9.7
Elec Res. 350°	10.2	8.1

VYCOR OUTGASSING

The rate of outgassing of Vycor at various temperatures is low compared to soft glasses.

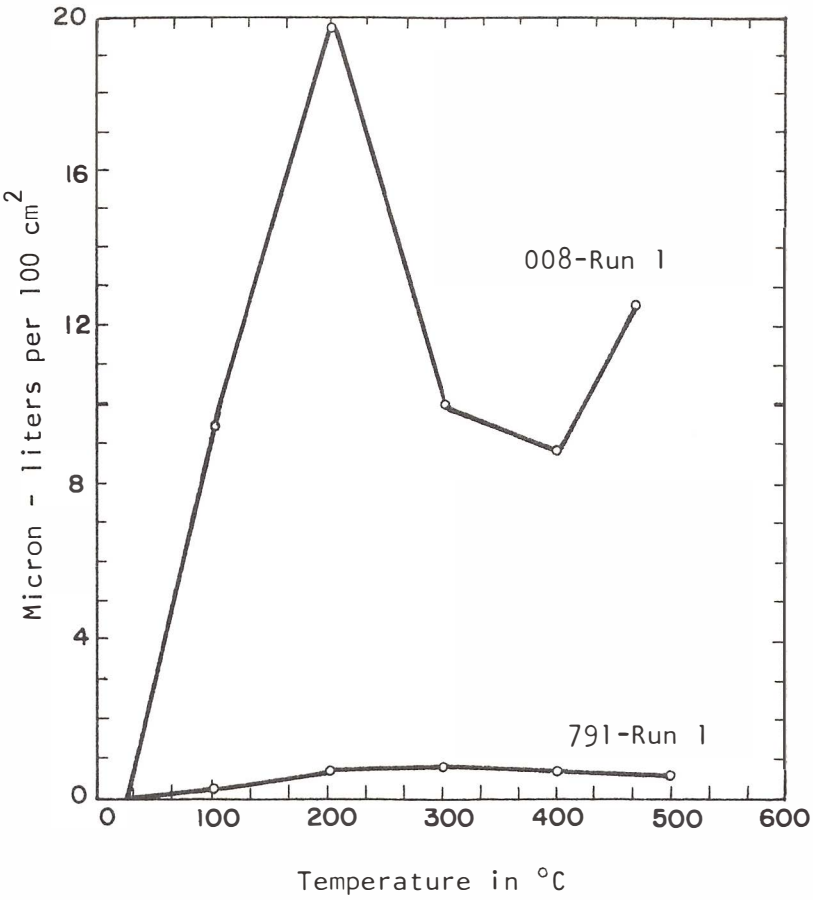


Figure 8

Comparison of Gas Evolution as a Function of the Temperature for a Corning Brand Lime Glass (008) and Vycor Brand Glass (791)

13.1.3 Selection of Quartz or Vycor

For long life lamps (>1000 hours):

Low water content quartz or Vycor type 7918 may be used.

For short life lamps (<1000 hours)

When UV transmittance is a factor use Vycor type 7917. UV radiation is extremely undesirable in the case of studio and theater lighting.

In all other cases, either quartz or Vycor type 7918 is acceptable.

There are many types of Vycor; the following table indicates the chemistry and physical properties of the different types.

Table I

CHEMICAL PARAMETERS* AND GENERAL PROPERTIES

	7910	7911	7912	7913	7915	7917	7921	7923	7918
Na_2O	< 200 ppm	< 200 ppm	< 200 ppm	< 300 ppm	< 20 ppm	< 60 ppm	< 100 ppm	< 60 ppm	< 300 ppm
B_2O_3 %	< 3.5	< 3.5	< 3.5	< 3.5	< 2.5	< 2.5	< 3.5	< 2.5	< 3.5
A Al_2O_3 %	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Li_2O %	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005
Fe_2O_3 %	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005
K_2O %	< .0005	< .0005	< .0005	< .003	< .0001	.0005	< .0005	< .0005	< .003
Va %	NA	NA	NA	NA	NA	0.06	NA	0.06	NA
$BETA_{OH}$	< .7mm^{-1}	< .4mm^{-1}	< .4mm^{-1}	< .4mm^{-1}	< .02mm^{-1}	< .3mm^{-1}	< .04mm^{-1}	< .07mm^{-1}	.04 .09
Expansion x 10^{-7}	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Annealing °C	910	910	910	1020	1040	1040	1040	1040	1020
*Transmittance/1mm									
1850Å	< 1%	NA	> 2%	NA	NA	NA	NA	NA	NA
2537Å	> 80%	NA	> 83%	NA	> 85%	NA	NA	NA	NA
3000Å	NA	NA	NA	NA	NA	< 32%	NA	< 32%	NA
2020Å	NA	> 85%	NA	NA	NA	NA	NA		NA
3600Å	NA	90%	NA	NA	NA	> 82%	NA	> 82%	NA
5800Å	NA	NA	NA	NA	NA	> 90%	NA	> 90%	NA

*These are not specifications but are normal levels
NA=Not Applicable

Note: The following trace elements appear in Code 7913 in these approximate quantities: Zr_2O_3, 0.25%; SnO, 300 ppm; TiO_2, 200 ppm; As_2O_3, 100 ppm.

Note: Code 7918 glass is designed for tungsten halogen lamp applications with controlled $Beta_{OH}$.

13.1.4 HARD GLASSES

Both fused quartz and Vycor are relatively costly to manufacture and both have two other features which are undesirable for use in lamps. Both require extremely high temperatures for bulb forming and sealing and both have very low thermal expansion which requires the use of special foil lead-ins which are costly and, because of their flimsy nature, are mechanically undesirable.

These shortcomings can be overcome by the use of hard glasses. The required characteristics of the hard glasses are:

Operating temperature high enough to support the tungsten-halogen cycle.

Low forming temperature for ease in lamp making.

Freedom from impurities that would interfere with the halogen cycle.

High thermal expansion to permit use of conventional moly lead-in wires.

Low cost.

There are a few aluminosilicate glasses which meet the requirements.

Corning 1702

Corning 1776

G.E. 180

G.E. 177 (for tungsten lead-in wires)

Osram 943

These glasses have strain points well above the practical minimum operating temperature required to support the halogen regenerative cycle yet can be formed and sealed at temperatures 400°C - 500°C lower than Vycor. The glasses are formulated from high-purity raw materials and should not contribute to atmosphere contaminants that would interfere with the halogen cycle. Although many lamp types have been designed to use hard glass, it does not follow that hard glass can be substituted directly for either quartz or Vycor in lamps that have been designed using those materials. It is probable that there are many applications where the lamp operating equipment and/or environment will

not permit the use of these glasses. It is also true that redesign will be required to permit their use in many existing lamp types. However, because of their unique characteristics, they permit the extension of regenerative cycle designs into new applications where they were formerly not practical.

13.1.5 Loss of Hydrogen from Lamp Envelope During Life

There is no question that hydrogen is a major factor in preventing bromine attack of tungsten in cooler parts of lamp such as leads and supports. Hydrogen is added to fill gas via the halogen dose. The loss of hydrogen during life is a lamp life determining factor. This problem was studied by Karl Lodue at Manchester HID Plant in 1976. A report was issued that showed that TAL analyzed "Good" and "Bad" long life linear bromine lamps were a function of the amount of hydrogen in envelope at end of life. The good lamps had more H_2. The problem is that all lamps started with the same amount of H_2 at zero life. This data is supported by Osram (Radium) information.

QUARTZ AND VYCOR

H_2 permeability of Vycor glass is about the same as that of pure fused silica in the range of 700 - 975°C. These temperatures are expected wall temperatures for quartz halogen lamps.

At high temperatures, silica glass is permeable to gases, in fact more so than ordinary silicate glasses. The Helium permeability is noticeable even at 180°C. Hydrogen permeability is noticeable above 300°C and Ne, N_2, O_2 and Argon above 900-1000°C.

The following table shows Gas Permeability of Quartz and Vycor at various temperatures.

TABLE 3

GAS PERMEABILITY ξ OF FUSED SILICA AT VARIOUS TEMPERATURES T FOR VARIOUS GASES

T	ξ { ordinary numbers in units of 10^{-10} cm³ (NTP) mm/sec-cm²-Torr; italicized numbers in units of 10^{-7} cm³ (NTP) mm/sec-cm²-atm }								
°C	He[1]	He[2]	Ne[1]	H_2[2]	D_2[4]	O_2[4]	Ar[2]	N_2[2]	N_2[6]
150	0.73 *0.56*	—							
200	1.39 *1.06*	—		0.022 *0.017*					
300	3.15 *2.4*	0.48 *0.32*		0.099 *0.075*					
400	6.15 *4.6*	0.99 *0.75*		0.37 *0.28*					
500	10.4 *7.9*	1.72 *1.3*	0.14 *0.11*	1.25[4] *0.95*					
600	16.4 *12.5*	3.0 *2.3*	0.28 *0.21*	1.43 *1.08*	1.7 *1.3*	<0.1 *<0.07*		0.065[7] *0.05*	0.066[7] *0.05*
700	21.9 *16.6*	4.25 *3.2*	0.42[4] *0.38*	2.52 | 2.1[4] *1.9* | *1.6*				0.132[8] *0.10*	0.146[9] *0.11*
800	28.5 *21.7*	5.5 *4.2*	0.81 *0.62*	4.25 *3.2*		Apparently less than for N_2	0.016[3] *0.012*	0.43 *0.33*	0.39 *0.30*
900	36.2 *27.7*	6.7 *5.1*	1.18 *0.9*	6.4 *4.9*			0.58[6] *0.44*	1.19 *0.90*	0.95 *0.72*
930	42[5] *32*	—	1.58[5] *1.2*	—			0.062[2] *0.047*		1.44[10] *1.10*
1000	45.4 *34.6*	8.4 *6.4*	1.63 *1.24*	10.0 *7.6*		(11)			
Atom-dia	1.95 Å	1.95 Å	2.4 Å	2.5 Å	2.55 Å	3.15 Å	3.2 Å	3.4 Å	3.4 Å

[1] TSAI, [2] BARRER, [3] BARRER, at 850 °C, [4] NORTON, [5] JOSSEN, [6] J. JOHNSON, [7] At 650°C, [8] At 750 °C: 0.268 (*0.204*), [9] At 750 °C: 0.271 (*0.21*), [10] At 950 °C, [11] According to NORTON, permeability at 700 °C for Ar, O_2 and N_2 should be less than 10^{-16} cm³ (NTP) mm / cm²-Torr-sec.

COMPARISON OF THERMAL AND MECHANICAL PROPERTIES OF HALOGEN LAMP ENVELOPE MATERIALS

	QUARTZ	VYCOR	GE 177	GE 180	1776	1720	1723	7725
SOFTENING POINT	1670	1530	1130	1020	944	915	910	770
ANNEAL POINT	1140	1020	865	805	749	712	710	550
STRAIN POINT	1070	890	885	755	705	667	670	515
EXPANSION	5.5	7.5	38	43	52.5	42	46	38
ELEC RES. 250^{o}	11.8	9.7	12.2	12.7	15.9	10.8	13.5	
ELEC RES. 350^{o}	10.2	8.1	10.5	11.1	13.0	9.0	11.3	
DENSITY	2.20	2.80	2.70	2.6		2.53		

Permeability is proportional to pressure gradiant and inversely proportioned to wall thickness. The total amount of hydrogen loss per unit time varies with bulb surface. That is for the same bulb wall temperature, wall thickness and pressure differential, the loss of H_2 from a big lamp envelope would be proportionally larger than a small bulb.

Computer analysis of H_2 permeation value at different temperatures indicates that.

Permeation of Hydrogen $\propto e^{.00439\ (T°C)}$ and is approximately equal to $0.12254\ e^{.00439\ (T°C)} \times 10^{-10}$.

The rate of loss of Hyrdogen in quartz halogen lamps can be controlled by the use of thick wall bulbs and bulbs large enough in diameter to run at minimum temperatures.

HARD GLASS

Glass is virtually impermeable to all gases except He, which will diffuse at elevated temperatures through silicate glasses in detectable quantities.

The gas permeability for various gases drops as the atomic radius of the diffusing gas increases. For example, the Ar permeability of Pyrex from 390° to 450° is $1/10^5$ of that for He in the same temperature range. The H_2 permeability of Corning ignition glass 1720 was found to be 4.5×10^{-13} at 665°.

For Comparison of H_2 Permeability

Temp	1720 Glass	Quartz
665°C	4.5×10^{-13}	2.27×10^{-10}

or the loss of hydrogen is approximately 1,000 times faster with quartz than with hard glass.

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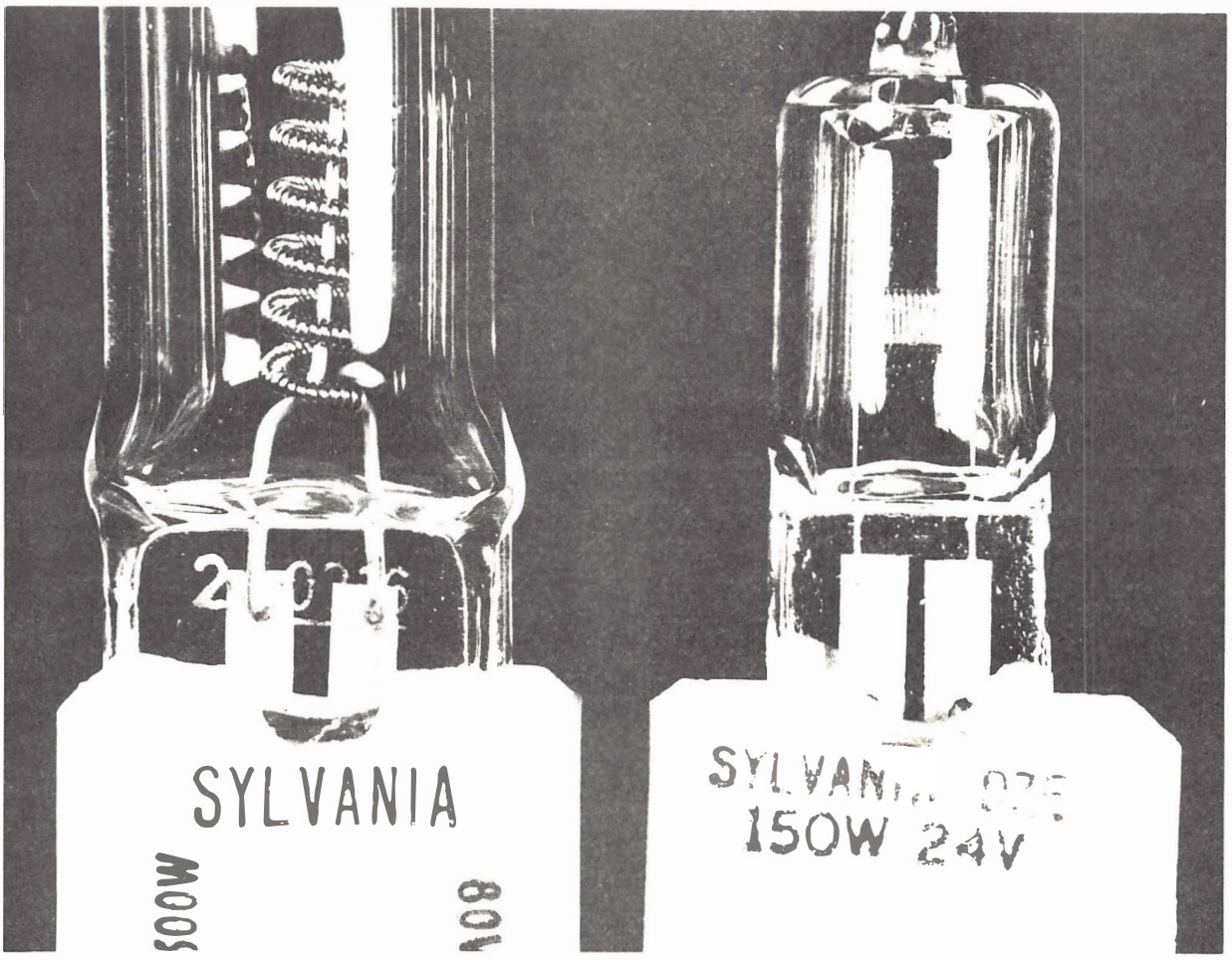
13.2 MOLYBDENUM

This metal has long been one of the basic materials for lamps because of its high melting point and great mechanical strength, similar to tungsten.

For halogen lamps, moly is used in two basic forms.

1. Thin ribbon for quartz and Vycor sealing.
2. Wire for outer leads in quarts lamps and in hard glass halogen lamps the entire inner lead and glass to metal seal is moly wire.



Photocopy-machine lamp and projection lamp

QUARTZ HALOGEN LAMPS

SYLVANIA EQUIVALENT - MO - 70

G.E. EC FINISH - Electrolytically etched to remove drawing lubricant and underlying oxides. High tensile strength but low ductility at room temperature.

SYLVANIA'S closest equivalent is MO-30.

MOLYBDENUM FEATHEREDGE WIRE

GTE Sylvania MH Molybdenum Featheredge Wire is used in high-intensity-discharge and tungsten-halogen lamps. It provides an air-tight lead into the lamp capsule to prevent degradation of the tungsten filament or emitter during operation. Molybdenum has good sealing properties for the housekeeper type seals to molybdenum and quartz. The tapered edge-configuration precludes "leaker paths" into the lamp envelope.

GTE Sylvania MH Molybdenum Featheredge Wire is made from Potassium doped 99.90% pure round wire which is rolled and electrolytically etched. Rigid control of this sequence results in a clean wire with uniformly tapered edges which are free of splits and burrs.

Width		Thickness	
mils	mm	mils	mm
50.0-225.0	1.27-5.71	0.80-3.00	0.020-0.076

Maximum edge thickness of 0.20 mils (0.005 mm).

	Width	Thickness
mils	89.0	1.30
mm	2.26	0.033
mils	121.0	1.30
mm	3.07	0.033
mils	183.0	1.30
mm	4.65	0.033

TOLERANCES

Thickness

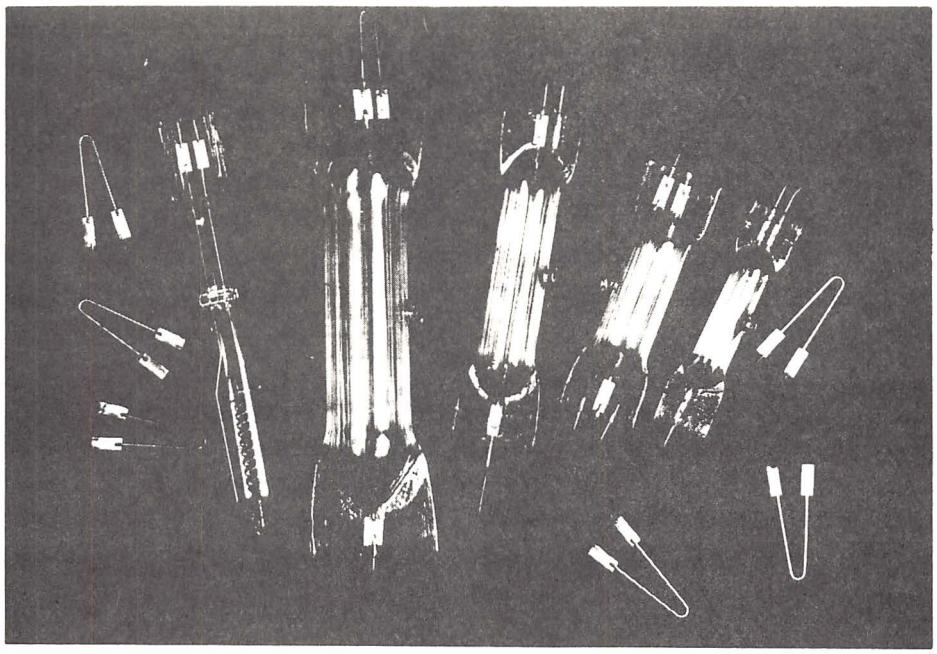
Less than 2.00 mils thick - $\pm$ 0.10 mils

2.00 mils thick and above - $\pm$ 0.20 mils

Width

$\pm$ 5.0 mils is standard

Tolerances down to $\pm$ 3.0 mils are available upon request.



Molybdenum Featheredge Wire in a tungsten-halogen lamp-capsule and in several high-intensity-discharge arc-tubes.

GE and SYLVANIA EQUIVALENTS

GE	SYLVANIA
KW	MH
R	MO

For featheredge quartz sealing ribbon, the best quality material is ribbon folled from 3% line etched KW wire. This material can be purchased from:

H. Cross, Inc.
363 Park Avenue
Weehawken, New Jersey
07087

13.2.2 TYPICAL SPECIFICATION FOR MOLY SEALING RIBBON

I. SUPPLIER: H. Cross

II. SPECIFICATIONS:

1. Shall be made of 99.90% moly 3% etched, type KW wire.
2. KW moly ribbon to be etched to the following dimensions:
   A. Using an L.S. Starrett Co. No. 221 micrometer, both edges of the ribbon must have a detectable thickness of less than .0002 inches.
   B. Center thickness to be 0.00105" $\pm$ .00005"
   C. Width - 0.089" $\pm$ .003"
3. Standard annealing process for single strand wire.
4. The crystal structure or grain shall run lengthwise with the ribbon.
5. Material shall be straight, not wavy, and the side wave of camber shall be kept to .125" for each foot, with no kinks, twists, or bends other than the curvature of spooling.
   A. Material shall be smooth, clean and free of surface impurities and discoloration.
6. Edges shall be free of splits, fissures and burrs.
7. Material shall be shipped on sulphur free spools in one continuous length, with ends securely fastened. The surface after spooling shall be protected or covered with sulphur free paper so as to keep the ribbon clean. The individual box for each spool shall be made of a sulphur free material.
8. Spools shall be properly marked with the supplier's name, size, length and type of material.
9. Length of ribbon on any spool to be between 500 and 1000 feet (preferably closer to 1000 feet.)

13.2.3 CHEMICAL BEHAVIOR OF MOLYBDENUM

Reagent	Reaction
HCl, H_2SO_4	cold, dilute and concentrated: virtually no reaction, hot, dilute and concentrated: light attack
HNO_3 (aqua regia)	cold, concentrated: slow attack cold, dilute: noticeable attack hot, dilute and concentrated: strong attack, dissolves completely
HF	Cold and hot: resistant
HF + HNO_3	strong attack, dissolves rapidly above 20°C
Alkalies	cold, aqueous KOH or NaOH: virtually resistant fused KOH or NaOH or alkali carbonates: (a) in air: slow oxidation (b) presence of oxidizing agents like KNO_3, KNO_2, $KClO_3$, PbO_2: powerful reaction, solution
Potassium nitrite and nitrate, NA_2O_2, $KClO_3$	reacts strongly with and dissolves in the fused reagent
NH_3	aqueous: slow attack gaseous: resists attack up to red heat
Carbons, (black, graphite, carbon)	carbide formation from 1100°C up, complete at 1300 - 1400°C.
Sulfur, dry	no effect up to 440°C, formation of sulfide at higher temperatures
Hg and its vapor	virtually resistant (less than 2 X 10^{-5}% soluble in Hg)
P	resistant up to high temperatures
B, Si	forms borides and silicides at very high temperatures
ZrO_2, MgO, Al_2O_3	reacts when in contact with the pure oxide above 1600°C

Reagent	Reaction
Air, oxygen	at room temperature: virtually no reaction at 300°C: begins to oxidize at 600°C: rapid oxidation to MoO_3 in damp atmosphere: deslueters
H_2O (20°C)	very light attack
Water vapor	rapid oxidation at red heat
H_2	inert up to melting point inert at low pressures up to 2400°C
N_2	forms nitride at very high temperatures
Oxides of N_2 N_2O, NO, NO_2	oxides to MoO_3 at red heat
CO_2	oxides above 1000-1200°C
CO, CH_4	carbide formation (Mo_2C) above 800°C
Halogens	fluorine: reacts at normal temperatures chlorine and bromine: attack begins at 250°C, marked at red heat iodine: no reaction on heating (800°C)
H_2S	reacts above 1200°C
SO_2	oxidation at red heat

(1) stages of oxidation:

MoO + MoO_3 black

MoO_2 violet to red, stable between 300 and 700°C

y = 6.74 g/ml

Mo_3O_3 + Mo_2O_5 violet to black

Mo_3O_3 whitish yellow, melting point 795°C;

y - 4.59 g/ml

MoO^8 vapor pressure at 500°C: ca. 10^{-5} Torr

600°C: 8.10^{-2} Torr

730°C: 8.10^{-1} Torr

800°C: 8 Torr

13.2.4 CHEMICAL CHARACTERISTICS OF MOLYBDENUM

Cleaning and Etching

1. Removal of oxides by cathodic treatment in dil. H_2SO_4 at approx. 100 amp/sq ft.
2. Dilute (8N) $NaNo_2$ or K(OH): anodic -- rapid etching
3. 1000 cc H_2O + 250 g (K(OH) + 0.25 g $CuSo_4$ (or $CuCl_2$) -- anodic, uniform etching
4. $NH_4(OH)$ + H_2O: uniform etching
5. 1000 cc H_2O + 305 g $K_3Fe(CN)_6$ + 44.5 g Na(OH) -- rapid etching
6. 50 pts HNO_3 + 30 pts H_2SO_4 + 20 pts H_2O at 900°C -- rapid etching
7. 95 pts conc. H_2SO_4 + 4.5 pts HF + 0.5 pt conc. HNO_3 + 18.8 g/liter Cr_2O_3 - 10 sec at 90°C for etching prior to resistance welding or braxing with tantalum foil.

13.2.5 TYPICAL SPECIFICATION FOR OUTER LEADS

I. Supplier

A. GTE SYLVANIA, INC.
Towanda
Pennsylvania

II. Material

A. Moly - MO-70 or MH-70

III. Specifications

A. Wire diameter: .030 $\pm$ 2%.

B. Tensile strength index to be between 47 and 57.

Index is defined as $\frac{L_{lb}}{M_w}$

Where L_{lb} = Breaking load, expressed in grams at standard gravity

M_w = Mass of wire for 200 mm length, milligrams.

For material with specific gravity of 10.2 (such as moly) the above index can be converted to psi by the multiplication factor, 2900. Thus the range is 151,000 to 165,000 psi.

C. Wire must be free of splits, fissures, kinks and all surface contaminants.

D. Length - 300 to 500 meters per spool.

E. Wire must be wound on spools in continuous lengths with no kinks.

F. Spools shall be marked with size and length of wire and with supplier's name.

G. Wire shall not be underwound on spools.

NOTE: Any spools received underwound shall be rejected and returned for correct rewinding.

NOTE: MH Moly may be superior in some types because of Higher Recrystallization temperatures and 40% higher tensile strength at elevated temperatures.

13.2.6 MOLYBDENUM AS A CONSTRUCTION MATERIAL IN HALOGEN LAMPS

NOTE: The following data is not conclusive. However, there are strong indications that the life and other quality factors can be improved by selective use of doped moly as a construction material internally for all types of halogen lamps.

Consider the following data:

1. Philips U.S. Patent #3,538,373

"When in lamps containing iodine as carrier gas all parts except the filament are made of moly. The bulb often blackens in operation. In such cases the moly probably binds an excess quantity of the oxygen required for a satisfactory operation of the cycle."

"If, however, in similar lamps containing as carrier gas bromine and/or chlorine and hydrogen, all the metal parts in bulb except the filament are made of moly, the lamp remains clean till the end of its life."

"It has been found, however, that in bromine and chlorine lamps, moly is more or less strongly attacked in accordance with the temperature the moly parts in the lamp attain by radiation, by convection or by thermal conduction. This does not give rise to blackening of the bulb wall."

"However, the life of the lamp may be shortened owing to the attack. The moly converted into a halide may be deposited in the form of whiskers on or in the proximity of the filament and give rise to short circuits."

2. Handbook data indicates that moly reacts with halogen as follows:

   Fluorine - Reaction at room temperature
   Chlorine - Reaction at 250 - 300°C
   Bromine - Reaction at 300 - 500°C
   Iodine - No reaction below 500 - 800°C.

3. The temperatures above which moly will not be be attacked are about the same as for tungsten.

   Chlorine - Above approximately 2500°C
   Bromine - Above approximately 1700°C
   Iodine - Above approximately 1200°C

   There is no doubt that moly and tungsten react to halogen in the same manner and are transported by same mechanism.

   W or MO + Halogen $\xrightarrow{>400°C}$ Metal Halide

   W or MO Metal Halide $\xrightarrow{>1700°C\,(Br)}$ W or MO + Halogen

4. Moly is not used for internal parts in quartz iodine lamps because it has been found to be a cause of lamp blackening.

   Moly is not used in quartz bromine or quartz chlorine lamps either. Probably because of proceeding iodine historic problems.

5. HARD GLASS BROMINE LAMPS USE MOLY WIRE LEADS ATTACHED DIRECTLY TO THE FILAMENT.

(See Figure 13.2.0) Page 201

6.. Not only do hard glass bromine lamps use moly, some types of moly have been found to improve the quality of hard glass bromine lamps.

GE PATENT #4,015,158

The object of the invention is to make an improved long lived tungsten halogen lamp using bromine for the regenerative carrier gas and containing inner leads and supports of molybdenum.

Our invention resulted from attempts to replace tungsten by more ductile molybdenum for the inner leads and filament supports in a tungsten bromine lamp. Standard grades of molybdenum are capable of from 6 to 10% elongation. We used molybdenum wire which is better than 99.9% molybdenum and which has been surface-etched and annealed in order to improve its ductility to a minimum of 15% elongation. The surface etching serves to remove impurities and in particular iron which are much more concentrated at the surface than in the core of the wire.

The high ductility molybdenum wire gives better clean wall performance, that is substantially no wall blackening by tungsten deposit at the bromine concentration formerly used.

WE HAVE NOW FOUND AN UNEXPECTED ADVANTAGE OF LONG USEFUL LIFE FROM THE USE OF SUCH HIGH DUCTILITY MOLYBDENUM IN A LAMP WHEN THE PROPORTIONS OF THE BROMINE OR BROMINE-PROVIDING COMPONENT ARE REDUCED TO ACCOMODATE THE HIGHER PURITY MATERIAL.

This bromine must be present as part of a fill gas comprising nitrogen which serves as an arc suppressor, and an inert gas such as argon. Molybdenum leads react with bromine and any oxygen present faster than tungsten leads and accordingly the amount of bromine had to be reduced to compensate for this faster reaction. In a lamp wherein the wall temperature immediately surrounding the filament is at least about 700°C and the cold spot temperature at the ends of the envelope is at least about 350°C, the useful range of bromine or bromine-providing component extends from 1.6×10^{-8} to 8.0×10^{-8} gram atoms per cubic centimeter of envelope volume.

Commercially available molybdenum wires known as type R, 99.95% molybdenum, and type KW, 99.90% molybdenum, were originally tried as substitutes for tungsten. Although less expensive than tungsten, these grades of molybdenum are comparatively brittle having a percentage elongation varying between 6 and 10%. With this degree of brittleness or lack of ductility, it was difficult to manufacture the mounts on high speed equipment due to fracture of the molybdenum at the clamps. We then used molybdenum wire which has been surface-etched and annealed to improve its ductility and which is capable of at least 15% elongation without rupture.

When the tungsten is replaced by molybdenum for the inner lamp parts exclusive of the filament, there are chemical reactions taking place involving molybdenum with bromine, oxygen, hydrogen and carbon, in addition to the usual ones involving tungsten with the same elements. We found that the concentration of bromine required in a lamp using surface-etched high ductility molybdenum needed to be reduced. Surprisingly, when the gas fill including the bromine concentration was optimized for the new high ductility molybdenum a great improvement in lamp life was obtained. Whereas previously, lamp lives of 3500 hours were considered excellent, lamp lives of greater than 4000 hours became the rule and lamp lives up to 6000 hours were measured.

(The bromine dose was methyl bromide (CH_3Br) d.d.)

The lower limit in the permissible bromine concentration above is determined by the amount of tungsten which can be tolerated on the bulb wall. With less than 1.6×10^{-8} gram atoms of bromine per cc. the lamp blackens after a number of hours of operation. However, the upper limit of 8.0×10^{-8} gram atoms per cc is determined by etching of the inner molybdenum conductors rather than by excessive degenerative cycle activity as in an all-tungsten lamp. Typical molybdenum lead etching which may occur with excessive bromine concentration is illustrated in Figure 2 and can be seen at 9', 10' and 11' on the innder conductors. While lead etching increases with increasing bromine concentration it will occur at all levels of bromine if too much oxygen is present. It is virtually impossible to remove completely the residual oxygen from the lamp envelope but it should be kept as low as possible and preferably

should not exceed a concentration of about 1.6 X 10^{-8} gram atoms per cc of envelope volume, such corresponding to 0.01% by volume at 3000 Torr.

Fig. 1

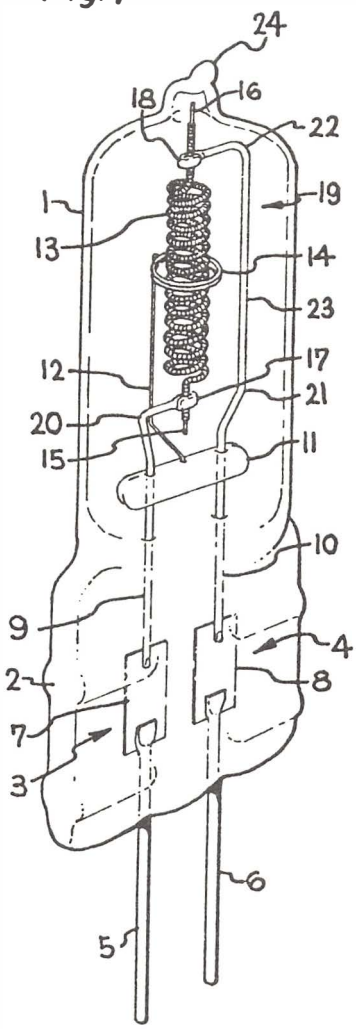
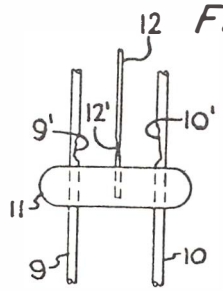


Fig. 2



We have analyzed the high ductility molybdenum wire used in our improved lamps and compared it with commercial grade low ductility molybdenum wire to determine the reason for the great increase in life obtained when the gas filling is optimized for such wire.

Commercial grade low ductility molybdenum wire is black wire in an as-drawn condition with only hydrogen annealing. High ductility wire is the same wire which has been subjected to a caustic etching wherein approximately 3% by weight of the material from the outer surface is removed.

Our analysis has shown that the significant impurity appears to be iron. In the as-drawn wire, iron is present as an impurity at the surface in a concentration which is probably in excess of 100 parts per million, but in the core of the same wire the concentration is only approximately 43 parts per million. When the same wire is caustic-etched to increase its ductility and the iron impurity concentration is again measured, it is approximately 50 parts per million at the surface and is unchanged in the core. Thus the effect of the treatment is to reduce the concentration of impurities at the surface to a level much closer to that existing within the core of the wire and in any event to a level less than twice that within the core.

Our study has led us to believe that high ductility molybdenum wire makes possible a longer life bromine regenerative cycle lamp because the wire surface is cleaner than in low ductility wire, and in particular because the iron impurity level is lower. This accords with the known deleterious effect of iron in a tungsten halogen lamp and which has always prevented the use of iron inleads and parts within the envelope.

In the lamps that we have made having improved lamp lives of 4000 hours or more, the molybdenum wire is at least 99.0% pure and has the concentration of iron impurity at the surface reduced to a level less than twice that within the core and preferably no greater than 1.5 times that within the core. The preferable condition corresponds to an iron impurity level not exceeding approximately 60 parts per million. Ideally, of course, the wire should be perfectly clean so that the iron impurity level at the surface is no greater than in the core, but such a condition is too difficult and expensive to achieve in practice. We believe that the lower impurity level allows us to use a lower level of bromine which results in the longer lives that we have observed in our lamps.

Experience at Boston Street, Salem, during the development of the hard glass halogen lamp for headlights proved that lamp performance was enhanced by the use of GE KW moly or GTE MH moly for the lead wires compared to moly mandrel wire or moly wire historically used for outer leads.

13.3 TANTALUM

Tantalum has been found useful in quartz halogen lamps as well as hard glass halogen lamps.

Ta has properties similar to MO and W in that it will enter into halogen cycles and be transported by some mechanism.

Ta has more resistance to bromine than MO or W. Ta is resistant to bromine to temperatures in excess of 500°C.

Ta is an excellent getter for hydrogen, oxygen, nitrogen and carbon. Ta is used as a support material in tubular quartz heat lamps. Ta is not used in iodine lamps because it reacts with iodine.

Ta reacts with bromine at lower than indicated temperatures at a low rate. Then Ta is substituted for Pt in lead assemblies, after a hundred hours of burning, the Ta is gone and weld is lost. The seal temperature is less than 350°C. The Ta has been converted to a gaseous metal halide during operation of the lamp.

13.4 SPECULATIVE CONCLUSIONS REGARDING MOLY AND Ta

1. In the case of Ta, the lamp improvement is due to gettering of hydrogen and oxygen. This appears to be the same results as found by putting zirconium in a halogen lamp. Thorn U.S. Patent #3,644,773, Westinghouse U.S. Patent #3,821,585, Philips U.S. Patent #3,829,731 and Philips German Patent #2,950,609 (June 1980).
2. The reason for black lamps when moly is used in iodine lamps and clean lamps when moly is used in bromine lamps is not known for sure. A reasonable assumption would be that higher bulb wall temperatures are used in iodine lamps. If the bulb blackening in the iodine lamps is due to deposited tungsten, it follows that the iodine dose is too low or is being depleted by combining with the moly. The Philips patent assumption that the moly was gettering oxygen and thereby decreasing the efficiency of the iodine transport cycle does not seem justified.
3. The reason for improvement in performance in hard glass halogen lamps and quartz halogen lamps by use of KW or MH moly in place of

MO types is not clear at all. GE claims that improvement is due to reduction of iron which could tie up or interfere with halogen cycle. The argument is that less bromine would be needed if no bromine was lost to the iron.

The use of KW in Sylvania hard glass halogen lamps resulted in less "activity." That is less whisker growth in first turn area like that experienced in a water cycle. The addition of Ta as the same observed result -- reduction of oxygen by gettering. However, the improvement is made by using 99.9% moly in place of 99.95% moly. The answer does not lie with moly itself. The improvement must be due to the 500 PPM added dopants. Potassium (K) for example is a getter for oxyten. K is released when either W wire or moly wire (MH) is heated the first time before recrystallization.

XXX More experimental work is required to sort out and confirm the reason why doped moly wire improves the lamp life over undoped moly wire. When understood, an overall technical improvement in all halogen lamps may be possible for use of moly in internal mount construction except for filament. In some lamps a cost reduction will also result because moly is far less expensive than tantalum and tungsten.

13.5 TUNGSTEN

The internal lamp parts in nearly all halogen lamps is tungsten. This includes the filament, the supports and inserts. The exception is hard glass halogen lamps where the leads are doped moly (Sylvania MH or GE KW)

The filament has been determined to be the largest source of contaminents in halogen lamps. It has been reported that Philips D wire is satisfactory for Ch_2Br_2 doped lamps and unsatisfactory for HBr doped lamps due to water cycle problems. It has also been reported "We found a big difference in behavior between Ivry (French) wire and Philips wire. It seems that substances evaporate out of Ivry wire, so that it has same effect on the addition of oxygen to the fill gas of lamps made with Philips wire." "With Ivry wire, we find shorter life and more whiskers. This is true for HBr, less a problem for CH_2Br_2 and is not true for CH_3Br." The following tungsten treatments should eliminate most of the contaminates.

NOTE: These tungsten treatments are expensive and may not be necessary in all cases. When a lamp contamination problem exists and filament is suspect, these treatments should be tried and if problem eliminated, as many of treatment steps retained as necessary to control the problem.

The observations indicate the liberation from the coil of a variety of atomic species during incandescence. These atoms come from impurities originally present in the ore, which are not removed during the preparation of tungsten, or from impurities introduced during the processing of the filament; or they originate from the doping of the materal. The liberation of atoms from the coil during incandescence can also be traced by activation analysis of the coiled material before and after a burning period. The spectroscopic results clearly establish that different spectral patterns originate from filaments of different origin. The results further indicate the important influence of differences in the reactive transport gases.

Consequently the following three types of processes must be considered for the interpretation of the measurements.

i. Evaporation during the whole duration of incandescence: This will be the case for the atoms W and Mo, as follows from the results with the blank lamp (with only inert gas).

ii. Evaporation of atoms during short periods, e.g., at the beginning of the incandescence: The steady state of excited atoms in the hot zone around and within the filament is maintained by some kind of transport reaction primarily due to the presence of the reactive gas. In this case the impurity atoms interfere with the tungsten halogen cycle. This process may have important consequences for lamp behavior at low halogen concentrations.

iii. Chemical reactions due to the transport gas: The observation of the atoms Al, Cr and perhaps also Ti is attributed to the presence of carbon. These metals are present as oxides. The following mechanism is suggested: at low temperatures ($\sim$500°C) the initially present CH_2Br_2 is pyrolyzed. The resulting carbon precipitates onto the filament and subsequent reduction of oxides at high temperatures takes place.

The presence of potassium in the gas phase could not be detected (using the resonance line at 766 nm). However, K comes out of the filament by heating in vacuum, as is well known from mass spectroscopy.

The filament has been identified as the chief source of impurities in well made halogen lamps.

The tungsten wire contains dope elements as well as impurities. During incandescence, dope elements and impurities may be liberated. The spectrum from 385 nm to 435 nm of a lamp filled with CH_2Br_2 has been evaluated. This spectrum represents a superposition of the continuous spectrum of the tungsten incandescence and emission peaks of the atoms of Al, Cr, Fe, Mo, Ti and W in the gas phase.

Filing of the lamp with Br_2 results in a spectrum different from that of the CH_2Br_2 lamp. The Al lines disappear, while the Cr and Ti lines become weaker. The use of HBr results in a spectrum similar to that with Br_2.

13.5.1 TUNGSTEN LAMP WIRE

Line etched NS wire should be used. The wire may be black or cleaned for coil winding. Line etched wire is lamp wire which has been drawn to about 20 mils and then etched to remove all surface contaminates and roughness. Approximately 6% weight is reduced by the cleandown. The wire then drawn to finish size and left black for coiling purposes. The drawn surface is quite smooth and the drawing compound (lubricants) about 0.4% by weight will come off at annealing and sintering with minimum effort. The GE designation for such wire is 218BLE (Black) or 218CLE (clean).

13.5.2 COILED COIL MANUFACTURING

Primary coiling is done on an S81 machine using a molybdenum mandrel. Anneal the coil on mandrel at 1400°C at 22 1/2 feet per minute in wet hydrogen. The bubbler bottle water temperature should be between 50-55°C.

Second coiling is done on a C-173 machine.

Coils are heat treated in boats at 1500°C in wet hydrogen for ten

minutes. The bubbler bottle water temperature should be between 50-55°C. Cool for ten minutes.

Molybdenum mandrel is dissolved out of the coils. Sufficient amounts of equal parts of nitric acid and sulfuric acid should be used to completely cover the coils. The coils are then boiled in a saturated solution of trisodium phosphate for fifteen minutes, rinsed thoroughly in hot tap water and dried. Coils are then given the coil etch process.

13.5.3 COIL ETCH PROCESS

1. Add six part of concentrated nitric acid to three parts of water. Add this to ten parts of concentrated hydrochloric acid.
2. Add the mixed acids to the vessel containing the batch of coils and heat to a boil.
3. Boil for fifteen minutes. The time is critical as a percentage of weight of the coils is lost. At the end of this time, the coils and vessel will be coated with a yellow tungsten oxide.
4. Rinse the coils in ammonium hydroxide to remove the yellow oxide coating.
5. Rinse several times in hot tap water followed by a distilled water rinse.
6. Repeat steps 3, 4, 5.
7. Boil in distilled water for fifteen minutes.
8. Centrifuge the coils as specified.

13.5.4 SCREW LEG MANUFACTURING

Coiling is done on a C-173 machine after which the coils are hand cut to obtain one good coil leg with approximately four turns in the coil body.

Coils are then boiled in a saturated solution of trisodium phosphate for 15 minutes and thoroughly rinsed in hot tap water. The coil etch process (See Sec. 13.5.3) is then done using the method as described previously except that in place of centrifuging, the coils are rinsed in alcohol and dried under heat.

13.5.5 SCREW ON COIL - IF USED

Coils are made on an S81 machine using molybdenum mandrel and are cut to about 6 inches in length.

Coils are heat treated in boats at 1130°C in wet hydrogen for 10 minutes. Bubbler bottle water temperatures should be between 50-55°C.

Molybdenum mandrel is dissolved out of the coils. Coils are then boiled in a saturated solution of trisodium phosphate for 15 minutes, rinsed thoroughly in tap water and dried.

Coils are then given the coil etch process (See Sec. 13.5.3) as described previously.

13.5.6 SLIP OVER COILS

Coils are made in an S81 machine and are cut into 6 inch lengths. Molybdenum mandrel is dissolved out of the coils.

Coils are heat treated in boats at 1130°C in wet hydrogen for 10 minutes. Bubbler bottle water temperature should be between 50-55°C.

Coils are then given the coil etch process (See Sec. 13.5.3) as described previously.

Slip-over coils are inserted on the leg and welded and cut to the length required, and then welded to the molybdenum ribbon.

The assembly is then heat treated at 1500°C in dry hydrogen for 10 minutes.

13.5.7 COIL STABILIZING

The filaments are heated in vacuum to 2500-2700°C for 1 to 4 hours. Coils are supported on tungsten rods, etc.

13.5.8 MOUNT TREATMENT

The finished mount assembly -- filament, supports and lead assemblies -- are heat treated at 1500°C for 10 minutes in dry hydrogen.

All mounts, just prior to sealing, are heat treated at 1130°C for 10 minutes in dry hudrogen. Heat treating should be done just prior to sealing and only a sufficient amount for each day's use. Mount stocks should be kept in heated cabinets.

This treatment has at times been extended to 16 hours in wet hydrogen, followed by 1/2 hour treatment at 2700°C in vacuum. (Complete mount with filament supported by tungsten mandrel).

With no intentional additions, carbon monoxide cannot be detected in lamps so treated, and lamp blackening occurs. This is taken as an indication of effective purification. If the high temperature treatment is omitted, approximately 2 Torr of carbon monoxide are obtained, and the lamp remains clean. It is assumed that the required carbon and oxygen has been evolved from the less clean filament. 2-4 Torr of carbon monoxide are required for some lamps; blackening occurs below 2-3 Torr and life is shortened by concentrations higher than 6 Torr.

NOTE: When dry H_2 is specificed, pure H_2 should be used -- not disassociate NH_3, which has a hydrocarbon impurity level.

13.5.8 EFFECT OF EXTENDED COIL TREATMENTS

Carbon and Oxygen in the coil has a large influence on the halogen cycle and sag resistance of the tungsten coil. The following data shows the change in carbon and oxygen content of coils processed with the standard treatment and extended variations.

A. Standard Process for Halogen Coils

A. Annealing at 1500°C in wet hydrogen.

B. Secondary treat in boats at 1180 - 1675°C in dry hydrogen for 10 minutes.

C. Stabilize in Vacuum at 2450°C for one minute. Coil supported on tungsten Rods.

This treatment results in 1 ppm carbon and 10 ppm oxygen impurity

B. Standard Process (A) plus 1675°C 8 hour wet dissociated NH_3 bake

Carbon 2 ppm Oxygen 60 ppm

The additional carbon could only have come from the dissociated NH_3

as an impurity. The additional oxygen is due to the dissociated H_2O in the wet hydrogen.

C. Standard Process (A) + (B) + Vacuum Stabilize

Carbon 2 ppm Oxygen 17 ppm

The vacuum stabilizing reduced the oxygen significantly but had little or no effect on the carbon.

D. Standard Process (A) + (B) + 8 hour dry dissociated NH_3

Carbon 3 ppm Oxygen 41 ppm

The dry dissociated NH_3 significantly reduced the oxygen, but increased the carbon. The increase in carbon can only be due to a hydrocarbon impurity in the dissociated NH_3. The resulting oxygen being higher than Standard Process (A) is due to inefficiency of "dry H_2" in reducing WO or removing absorbed oxygen.

E. Standard Process (A) + (B) + 8 hour dry H_2 Bake + Vacuum Stabilize

Carbon 1 ppm Oxygen 6 ppm

The vacuum Stabilizing is a major factor in reduction of carbon and oxygen but only after extended wet and dry dissociated NH_3 baking.

The Standard Process effect on carbon and oxygen is as follows:

a. Wet dissociated NH_3 anneal (1500°C)
   Carbon 11 ppm Oxygen 54 ppm
b. Sintered in dry dissociated NH_3 1675°C
   10 minutes + a.
   Carbon 12 ppm Oxygen 20 ppm
c. a + b + Vacuum stabilized at 2450°C
   Carbon 1 ppm Oxygen 10 ppm

The lowest carbon (1 ppm) and oxygen (6 ppm) contents resulted from the most extended treatment, including 8 hours wet plus 8 hours dry dissociated NH_3. However, the standard treatment, involving 10 minutes in dry dissociated NH_3 produced similar results with 1 ppm carbon and 10 ppm oxygen.

Individual treatment steps were found to have the following specific effects.

The 10-minute, 1675°C, dry dissociated NH_3 sintering treatment alone decreases oxygen by a factor of about 2.5.

The 8-hour, 1675°C, dry dissociated NH_3 (after the 8 hour 1675°C wet dissociated NH_3) treatment decreases oxygen to about the same degree (factors of 1.5-3).

The 1675°C treatments in dry dissociated NH_3 seem to decrease carbon for subsequently vacuum stabilized wire only, by factors of 3-5. In contrast, there seems to be no significant effect where the wire is not stabilized.

The wet dissociated NH_3 treatment for 8 hours at 1675°C increases oxygen by factors of 1.7-3.

The same treatment seems to decrease carbon substantially, i.e., up to a factor of 6. There is considered to be no significant difference between 1, 2, and 3 ppm carbon, since analyses are reported to $\pm$ 50% in this range.

The 2450°C vacuum stabilization decreases both carbon (x2-12) and oxygen (x2-7). This treatment seems to be the most effective single step in decreasing both carbon and oxygen, and its effect seems to be maximized when coupled with sintering at 1675°C.

Substantial decreases in Fe, Ni, and Cr also result from vacuum stabilization, which decreases the sum of all three elements from a mean of 72.2 ppm to 51.6 ppm.

The data also show that Fe increases during the extended (8 and 16 hour) treatments at 1675°C in dissociated NH_3, both wet and dry. The mean Fe of the extended treatment coils is 58.8 ppm, significantly (almost 95% confidence) higher than that of the short treatment groups at 39.5 ppm.

There is also some indication that the coils may also pick up some Fe even during the 10-minute treatments at 1675°C. This Fe might come from the catalyst used in dissociating the NH_3 - a view supported by the fact that Ni + Cr do not increase, but actually seem to decrease somewhat (14.8 to 10.7 ppm) while Fe increases. This contrasts with the effect of 2450°C vacuum stabilization, where all three elements respond uniformly and decrease together. Thus, the substantial initial decrease

in Fe from 49 ppm to 28 ppm after standard coil processing seems to be a real effect, as is the subsequent rise to a maximum of 69 ppm, reflecting Fe pickup during extended processing, not offset by the purifying effect of vaccum stabilization.

13.5.10 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

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   Available from D. Dayton, GTE Sylvania, Ipswich, Massachusetts.

2. Emission Lines in the Spectra of Halogen Incandescent Lamps by W.J. Van Den Hoek and F.G. Berns.
   N.V. Philips Lighting Research and Technology, Vol. 7, No. 2 - 1975.

3. An Investigation into the Nature of Iron Contamination on the Surface of Tungsten Wire.
   Thorn Lighting, LTD., 1971.
   Available from D. Dayton, GTE Sylvania, Ipswich, Massachusetts.

4. Report on Extended Coil Treatment for ELH Lamps.
   Dr. E. Possmore, GTE Sylvania Lighting Center, Danvers, Massachusetts. 1980.

5. The Influence of Metallic Impurities on the Tungsten Bromine Regenerated Cycle of Linear Quartz, Bromine Lamps, by L.N. Yannopoulos and A.L. Wolfe. Westinghouse, Journal of Applied Physics, Vol. 50, No. 9, September 1979.

6. The Role of Impurity Metals in Halogen Lamps, by I. Hangos and L. Bartha.
   Acta Technica Academiae Scientiarium Hungaricae, Tomus 78 (3-4), pp. 405-416 (1974).

13.6 FILAMENT GEOMETRY

The shape of geometry of the filament is determined by the length of the filament, the size of the bulb, the wattage and the application of the incandenscent lamp.

Table VI shows some common filament types and their typical applications. Figures 13.6.1, 13.6.2, and 13.6.3 show some additional types and the geometry of the light distribution that results from various geometric configurations.

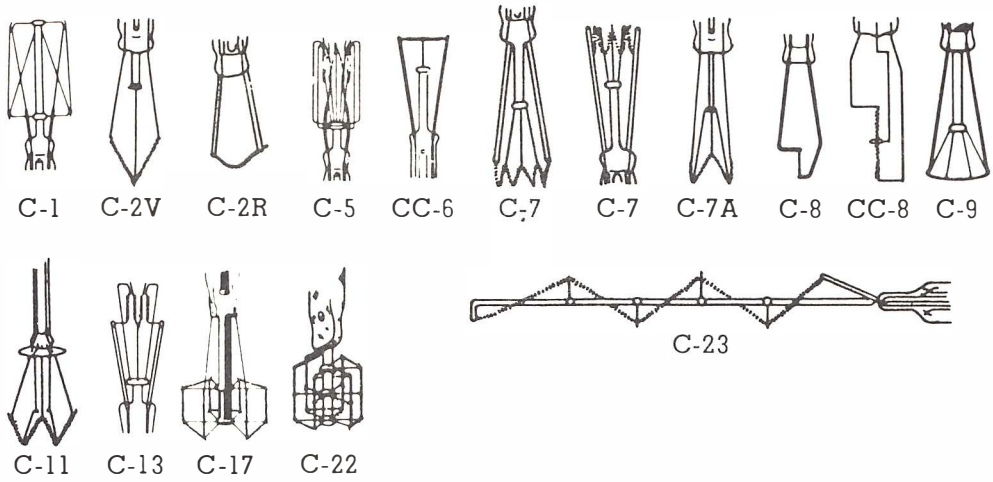


TABLE VI

VARIOUS INCANDESCENT LAMP FILAMENTS

Filament Designation	Description	Typical Lamp Using This Filament
C-1	Fairly long coiled filament, well supported.	15W, S-11, 75V, Train
C-2V	Fairly short coiled filament which requires one support.	6000 lumen, PS-40, Street Series
C-2R (Rounded)	Short filament, slightly rounded, requiring no supports.	30 volt, A-21 Street Railway
C-5	Concentrated filament for small light sources.	500W, G-40 Spot or Flood
C-6	Short coiled filament requiring few or no supports.	50W, A-21, 6 volt
CC-6	Short coiled-coil filament requiring few supports.	60W, A-19
C-7	Fairly long filament supported at top for base up burning.	10,000 lumen, PS-40, base up 20 amp., St. Series
C-7	Fairly long filament supported at bottom for base down burning.	10,000 lumen, PS-40, base down 20 amp., St. Series
C-7A	Long filament supported top and bottom for universal burning.	500W, PS-40, 230 volt
C-8	Coiled filament mounted along axis of bulb. May be elongated as in lumiline lamps.	25W, T-10, Showcase
CC-8	Short coiled-coil filament along axis of bulbs.	100W, A-19
C-9	Filament of average length, well supported. Semicircular. Also used for vibration service.	25W, A-19
C-11	Concentrated filament of some length. Well supported. "M" — shaped.	250W, G-30, Infrared
C-13	Monoplane filament, high concentrated for peojection equipment.	500W, T-20, Spotlight
C-17	Long filament requiring more than average number of supports.	100W, A-21, Rough Service
C-22	Long filament with extra supports for resistance to physical shock.	50W, A-19, Rough Service
C-23	Coiled filament mounted along axis of bulb and alternated along the length.	40W, T-8, Showcase

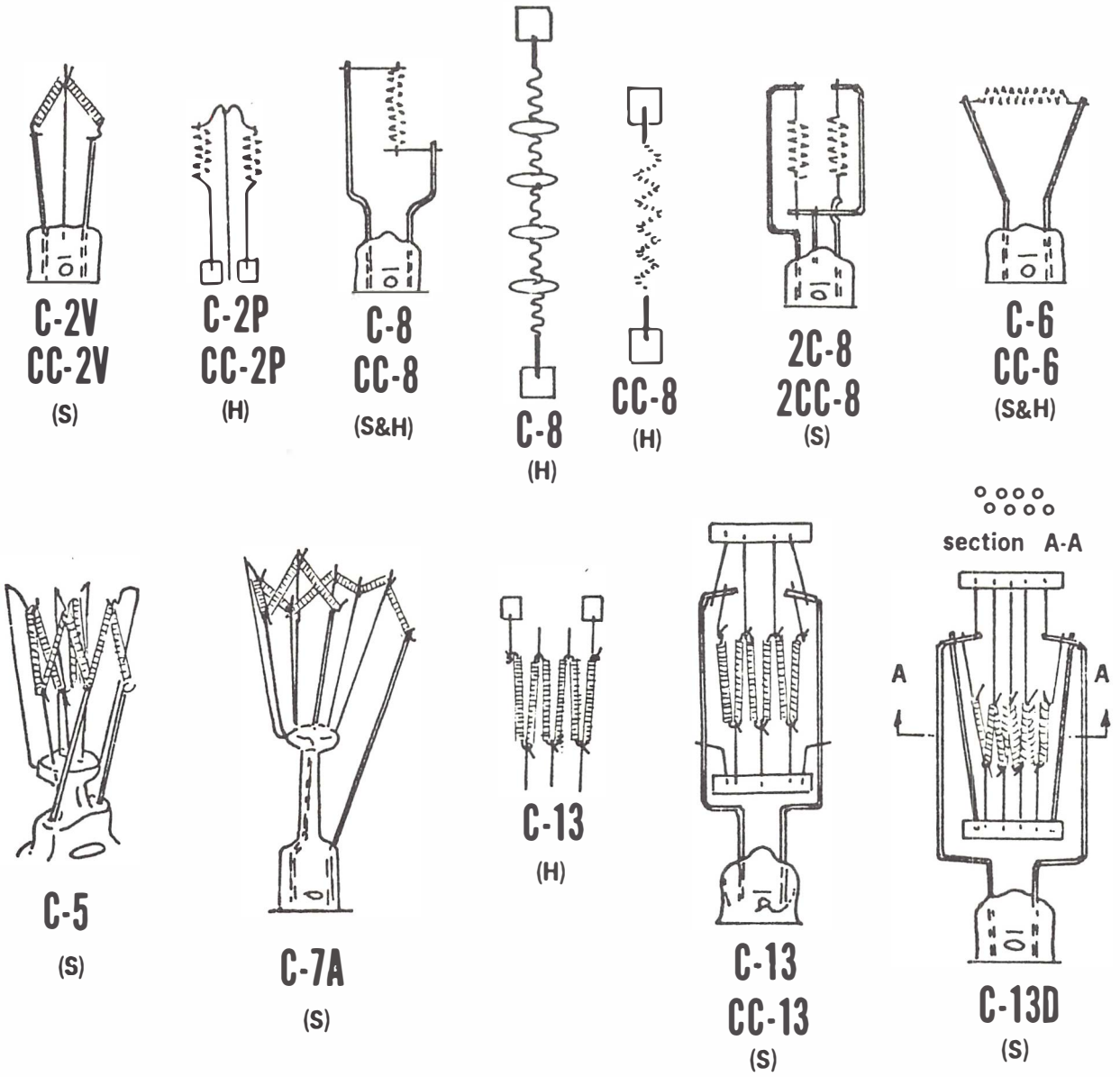


Figure 13.6.1

Filament forms most commonly used in lamps for studio lighting. They are identified by two-part designations: a describtive letter prefix such as "C" (when the filament wire is coiled before mounting), or "CC" (coiled coil), plus an arbitrary number or number-letter suffix that identifies the configuration of the filament and the supporting structure, and their relation to the lamp axis. The letter (S) or (H) indicate whether the particular filament form is primarily associated with standard (S) or halogen-cycle (H) lamps. Proportions of filaments and details of mount structures in specific lamps may vary considerably from the illustrations.

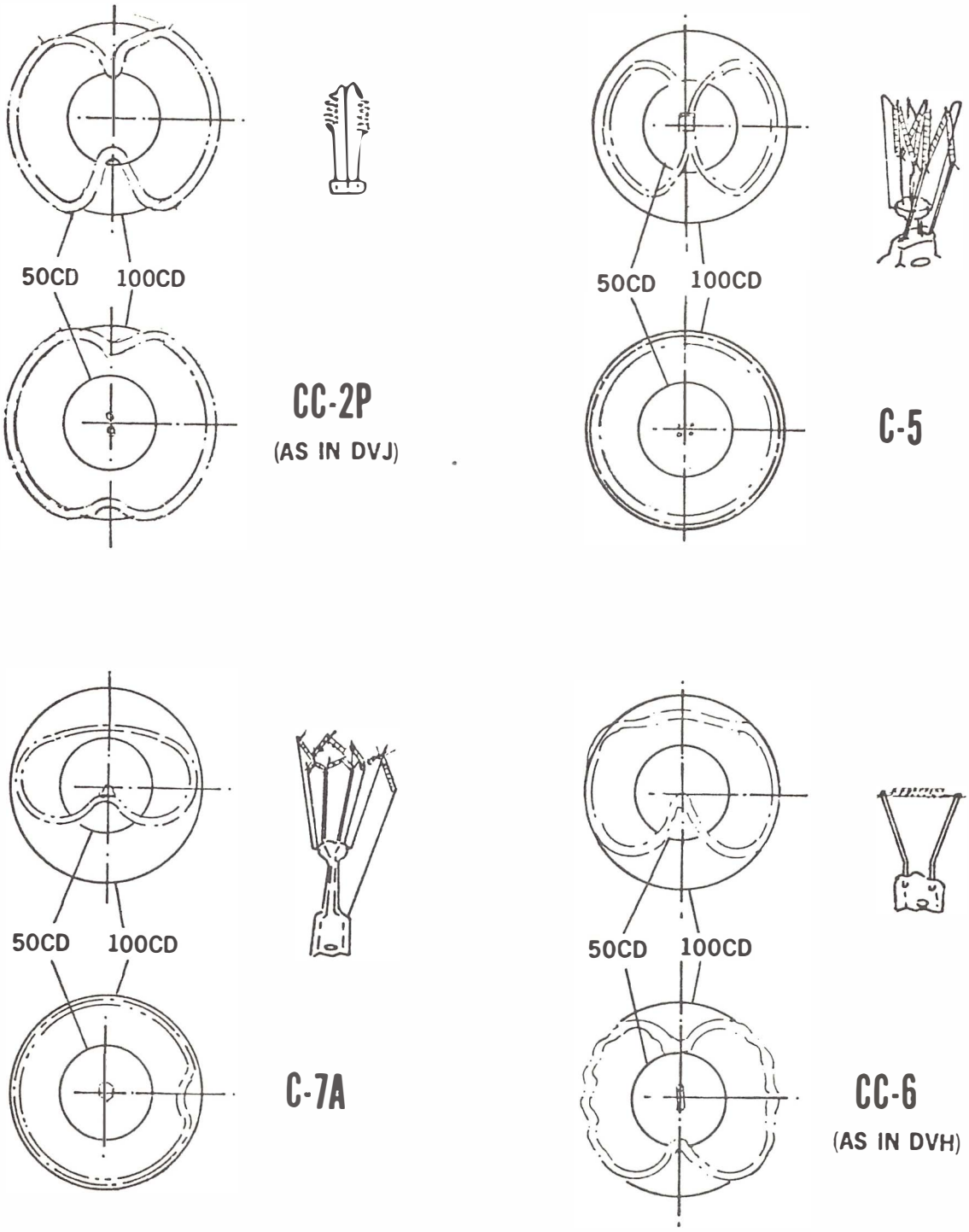


Figure 13.6.2
Generalized polar distribution of candlepower for several of the filament types of Figure 13.6.1. Circular reference lines indicate intensity values of 50 and 100 candelas per 1000 lumens of total emitted light. Angles of measurement are in plane of paper when filament is oriented as indicated in the center of each polar plot. Curves are of typical lamps with each filament form; specific lamp types may have considerably different distributions.

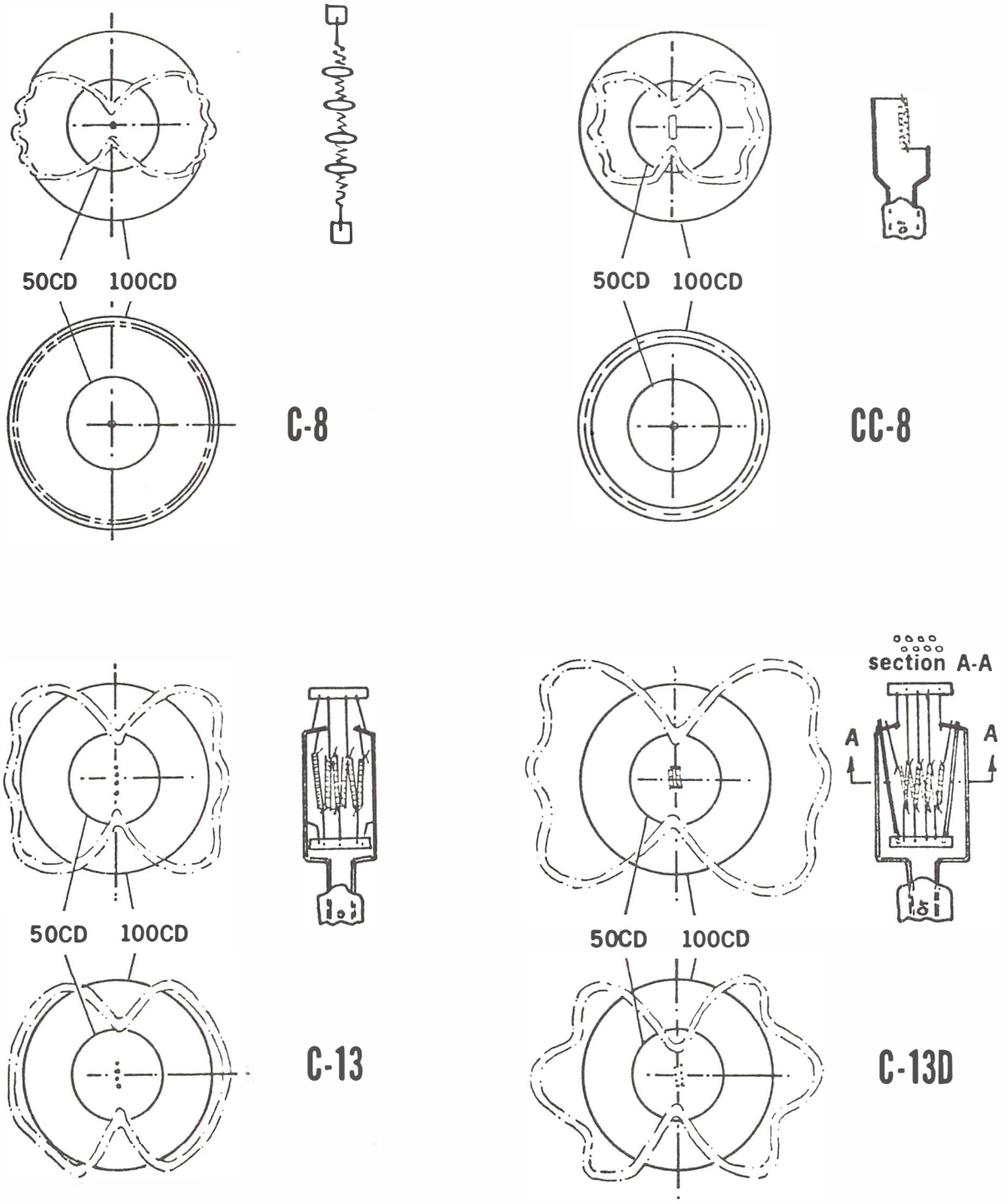


Figure 13.6.3
Generalized polar distribution of candlepower for several of the filament types of Figure 13.6.1. Circular reference lines indicate intensity values of 50 and 100 candelas per 1000 lumens of total emitted light. Angles of measurement are in plan of paper when filament is oriented as indicated in the center of each polar plot. Curves are of typical lamps with each filament form; specific lamp types may have considerably different distributions.

13.7 FILAMENT DESIGN

A halogen lamp is just another incandescent lamp from a filament design point of view. The coil temperature can be either higher or lower than common GLS lamps. The lamp fill pressure is usually higher and the bulb is smaller. The net result is less convection and more conduction of heat by the fill gas. This is offset by higher bulb wall temperatures. Generally there is a small correction in filament design as a result of these variables. However, for a place to start, consider the halogen lamp a GLS lamp and follow procedures in Chapter II Incandescent Lamp Design and Manufacturing Handbook by David R. Dayton. The correction from GLS data will be mostly due to the difference between measured Lpw and actual Lpw. On GLS lamps, the multible is about 1.1. In small halogen lamps, the multible can be 1.3 or more. Long linear lamp, the multible is about the same as GLS lamp.

13.8 FILAMENT SAG CONTROL

Halogen lamps are usually high wattage which means heavy coils with more unsupported weight. While it is true that the filament wire is bigger, the coil winding ratios remain the same. It is also true that sag occurs in GLS lamps and is not considered to be a life determining factor. The following are considerations regarding coil sag.

13.8.1 Wire Control and Coil Lot Testing

a. Wide variation in the sag properties of wire as received from the wire plant.

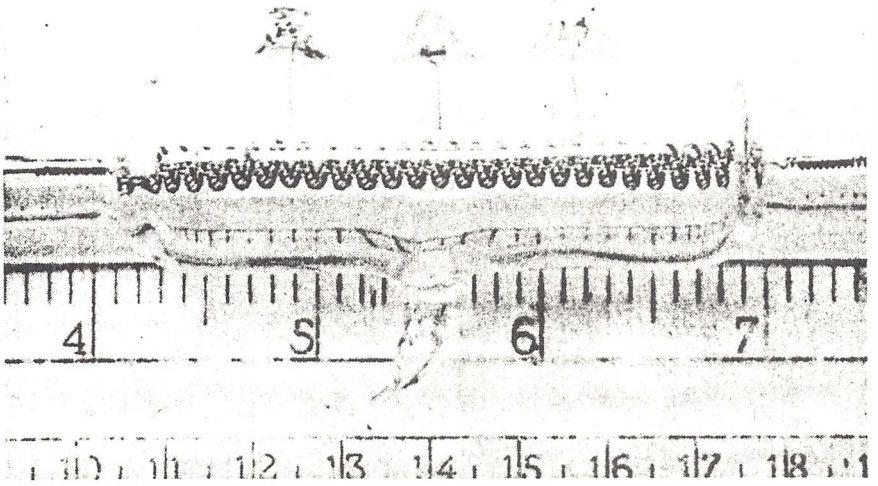
b. Placing limits on sag rating (hot tensile strength test) will reduce the amount of wire rejected but will not assure wire that does not sag.

c. There appears to be no difference in the sag characteristics of annealed and non-annealed wire if the sag ratings are the same. It must be pointed out, however, that annealed wire with low sag is difficult to find.

d. The operating temperature (3000-3600°K) of a filament has little, if anything at all, to do with the degree of sag obtained in wire with poor sag properties. It only governs the time required to sag a given amount.

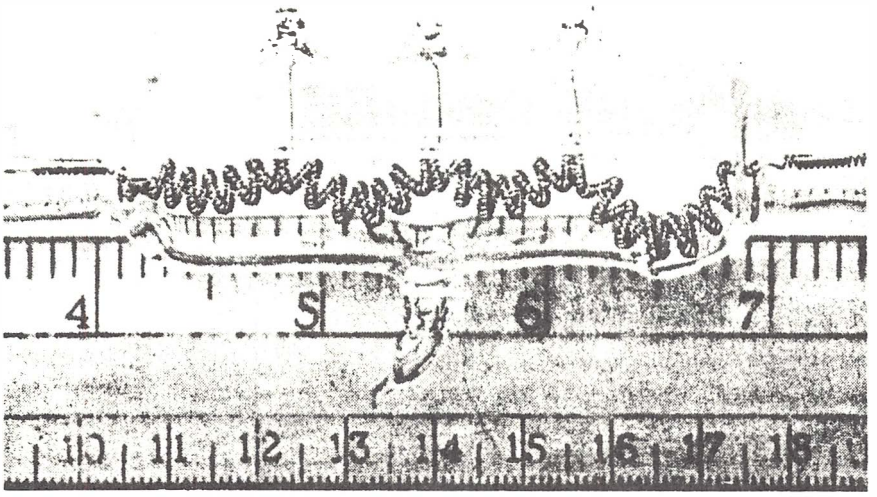
3. Coil lot testing and placing limits on sag ratings is the best first step in eliminating sag as a finished lamp problem.

(a)



BEFORE LIGHT UP

(b)



SEVERE SAG AFTER AGING

13.8.2 Methane Flashing

The phenomena of filament sag, associated with certain types of tungsten wire in coiled coil filament configurations operating in hydrogen bromide atmospheres, has been established beyond possible doubt.

It has also been established that this sag can be delayed or controlled, depending upon the operating temperature of the tungsten, by flashing the stabilized filament at about 1000°C in a carbonatious atmosphere, e.g., 1% methane in nitrogen. Under these conditions carbon is deposited on the filament in two forms:

1. A free carbon layer which is removed when the filament is raised to its normal operating temperature.
2. A firmly bound carbide.
3. Oxygen is one of the major variables because good lamps can be made to sag by adding oxygen to the fill gas.

For ELH, this involves heating of the lamp and filament, typically for six seconds at 55 volts, in an atmosphere of 1% CH_4-88%N_2. This is generally carried out in two separate steps, each followed by an exhaust and fill cycle. This treatment has been applied to several lamp types with short life problems besides ELH lamps, resulting in increases in life up to 90%, for example, for 240-volt, 800-watt, 50-hour DXX lamps, where the mean life was increased from 18 to 35 hours.

13.8.3 Chemical Correlations - Tungsten Ingot Compositions

These efforts included extensive attempts made to characterize good, i.e., sag-resistant vs bad or sag-prone wire by various factors including composition. Representative data, provided by the wire plant at Towanda, show average concentrations of several elements in ingots from both good and bad (or reject) lots of tungsten powder, Table 1. It can be seen that four out of the five elements are higher in the good lots than in the reject lots. Using the same data, normalized to 100% for good lots, the comparisons become more clearly evident, whereby it can be seen that the widest difference is for carbon, while, on the other hand, nickel shows little difference.

Thus, it appears that C, Cr, Fe, and K are all useful, perhaps even necessary, in providing sag-resistant tungsten wire. Continuing to use

data supplied by Towanda and from ELH lamp TBM evaluations at Winchester, the proportion of rejected ingots in each powder lot is shown, Figure 2 as a function of an empirical compositional parameter, representing the concentrations of the four elements: Cr, Fe, K and C, for which significant correlations appeared between averages for good and reject lots. A curve drawn through several of the data points delineates the regions of good wire, with relatively high concentrations of these elements, vs that where saggy wire occurs, although not all lots in the latter region are defective to the same degree.

Table I

Average Ingot Analyses, PPM

	Cr	Fe	Ni	K	C
Good Lots	9.1	35.6	21.8	56.3	7.6
Reject Lots	8.3	28.6	22.9	53.0	5.0

Average Ingot Analysis, Normalized

	Cr	Fe	Ni	K	C
Good Lots	100	100	100	100	100%
Reject Lots	91	80	105	94	66%

Partly as a result of such correlations, a minimum potassium content of 55 ppm has been specified for all future tungsten lots for ELH lamp wire.

13.8.4 Investigation of Oxygen Additives

Based on previous observations of water cycle erosion of saggy coils in short life lamps, it was concluded that oxygen might be another significant element involved in creep of tungsten wire. To further our understanding of coil sag, experiments were carried out at the Winchester plant by George Duggan. Various amounts of oxygen were added to the fill gas. The lamps were then burned for one hour at rated voltage, whereupon the coils were evaluated visually for degree of sag. For each group of ten ELH lamps, corresponding to a single oxygen concentration, the proportion of lamps showing moderate to severe sag was determined.

This parameter was then evaluated as a function of oxygen added for both ELH coils from good, i.e., TBM approved, and bad, i.e., TBM rejected lots. In addition, the CH_4 flashing treatment was evaluated for selected conditions. Typical results for ELH lamps, Figure 2A, show increases in the percent of saggy coils vs added O_2 for both rejected and good wire. It should be noted that little or no sag was found, even for rejected wire, until the added O_2 exceed 0.01%, whereupon the gap between good and bad wire increased up to 0.1% O_2 added. Above this concentration, sag in the good wire increased sharply with further O_2. Note also that the CH_4 flashed coils, whether from good or bad wire, showed substantially less sag at any particular O_2 addition, and that the distinction between good and bad wire essentially disappeared after CH_4 flashing. Selected, representative coils were then sectioned and polished for microscopic examination to determine if the factors affecting sag could be correlated with porosity and other miscrostructural phenomena.

NOTE: There is some current work (December 1980) on a new GTE wire for halogen lamps. The wire is designated AK. The major difference between AW and AK is the reduction in Nickel, Iron, Chromium and Moly in the AK wire. Present data indicate AK wire out-performs AW to some degree. The reduction in Ni, Fe, and Cr should be helpful in controlling the halogen dose throughout lamp life.

13.9 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

1. Effect of Oxygen and CH_4 Flash on Sag in ELH lamps by G.L. Duggan, GTE Electric Products, Lighting Center, Endicott Street, Danvers, Massachusetts.
2. Update on Sag in Tungsten, by Dr. Ed Possmore. Laboratory Report #LR-92, September 27, 1978.
   GTE Electric Products, Lighting Center, Danvers, Massachusetts.
3. Reactions of Oxygen with Pure Tungsten and Tungsten Containing Carbon, by J.A. Becker and R.D. Brondes, Journal of Applied Physics, Vol. 32, No. 3, March 1961.
4. The Reaction of Bromine and Oxygen with a Tungsten Surface, by Rouweler and Maagt, Philips Journal of Research, Vol. 33, Nos. 1 & 2, 1978.

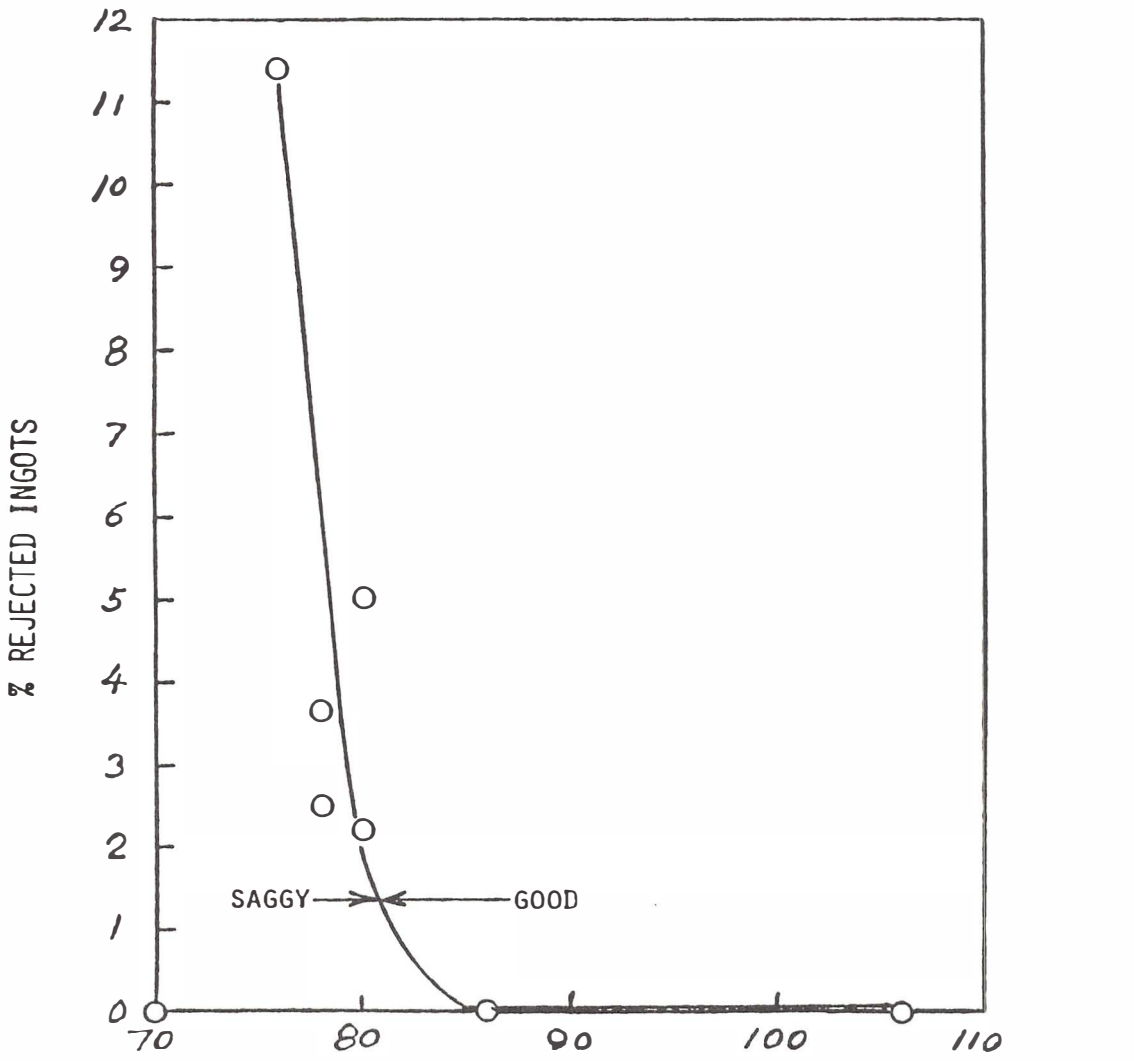
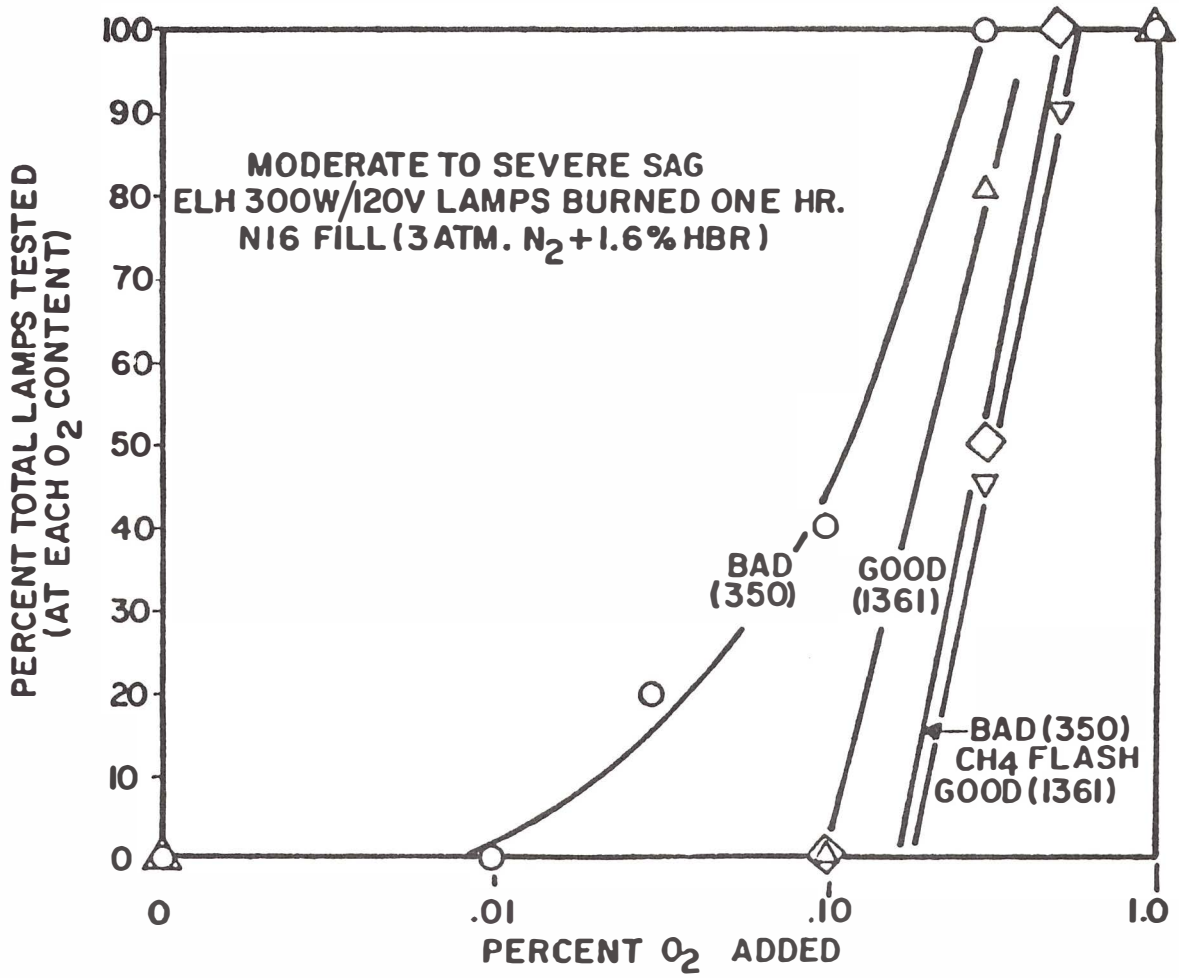

% REJECTED INGOTS
12
11
10
9
8
7
6
5
4
3
2
1
0
70
80
90
100
110
SAGGY
GOOD
CHROMIUM PLUS IRON PLUS 2 X (POTASSIUM-40) PLUS 3 X CARBON
CR+FE+2(K-40)+3C, PPM (INGOT ANALYSES)

FIGURE 2

FIGURE 2A


MODERATE TO SEVERE SAG
ELH 300W/120V LAMPS BURNED ONE HR.
N16 FILL (3 ATM. N_2 + 1.6% HBR)
PERCENT TOTAL LAMPS TESTED (AT EACH O_2 CONTENT)
100
90
80
70
60
50
40
30
20
10
0
BAD (350)
GOOD (1361)
BAD (350) CH4 FLASH GOOD (1361)
0
.01
.10
1.0
PERCENT O_2 ADDED

14.0 LEAD-IN SEALS

Moly is used for lead-in seals for all types of halogen lamps. However, the type and mechanism of moly to quartz or Vycor is very different from the moly to hard glass seal. The moly to quartz seal is an unmatched seal. That is the moly and quartz have very different expansion coefficients. The moly to hard glass is a matched seal.

14.1 QUARTZ TO MOLY SEALS

When the expansion of the metal does not match the glass, instead of wires or pins, thin ribbons are sealed through the glass.

The most commonly used quartz-metal seal is the molybdenum ribbon lead-through. The vacuum tightness of this seal is based on the fact that silica wets clean molybdenum and that the adhesion between the two is very strong, especially if the surface of the molybdenum is roughened by chemical etching.

The molybdenum ribbon required for the seal should be cut from foil. The ribbon may also be rolled from molybdenum wire.

The etching of the molybdenum ribbon may be carried out either by pickling in a solution of sodium or potassium hydroxide or by an immersion in a mixture of nitric and sulphuric acid, followed by a thorough washing.

The ribbons should be thin enough to avoid tensile stresses appearing in the quartz in a direction perpendicular to the plane of the ribbon. At the same time it should be thick enough to withstand the longitudinal stress set up in it, during the cooling of the seal. A molybdenum ribbon 0.01 mm thick withstands this stress if its width does not exceed 2mm; with a thicker ribbon the width may be made greater. It is possible to make successful seals using ribbons as thick as 0.1 mm if the thickness is suitably reduced for a distance of at least 0.5 mm from each edge, so that the cross section be elliptical with the thickness near the edge not exceeding 0.08 mm. Experience recommends ribbons with a thickness of about 0.02 mm and a width of maximum 5 mm, or thicker ribbons having the edges thinned down to about 0.015 mm.

Figure 14.1.1 shows a typical double and quartz halogen lamp with ribbon seals.

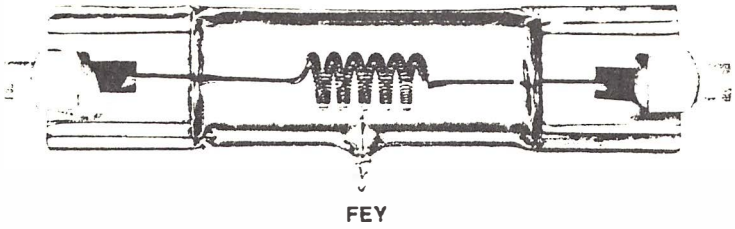


Figure 14.1.1

The current carrying capacity of ribbon seals is generally very high compared with rod, pin or wire lead-throughs of the same cross-sectional area. Fig. 14.1.2 shows the rated current for molybdenum ribbons (0.015 mm thick) sealed in quartz. A quick comparison with the maximum current permitted in wire (rod, or pin) seals (Table 14.1.3) shows that the cross-sectional area for the same current is about ten times less for the ribbon seals.

Fig. 14.1.4 and Table give the dimensions of some molybdenum ribbon seals.

Single ribbon seals are available only up to about 10A. For higher currents twin or multiple ribbon sales should be used.

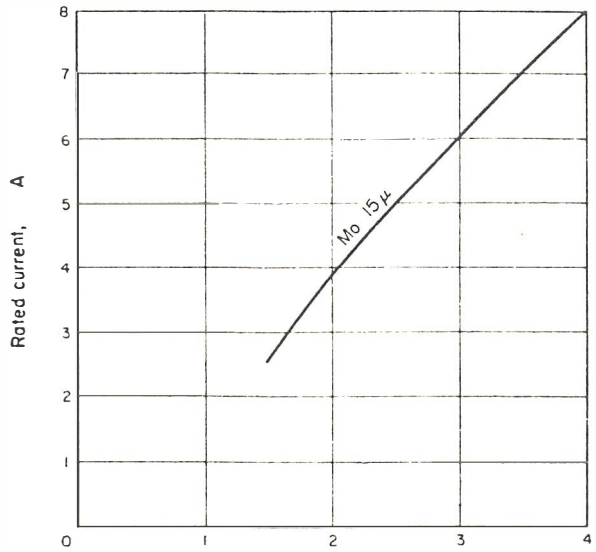


Figure 14.1.2
Rated current for molybdenum ribbons (0.015 mm thick)sealed into quartz

TABLE 14.1.3

MOLY WIRE SIZE DIA. in mm	MAX ADMISSIBLE CURRENT AMPS
0.33	2.68
0.4	3.3
0.5	4.0
0.6	5.0
0.7	6.0
0.8	7.0
0.9	8.0
1.0	9.8
2.0	35.0
3.0	50.0
4.0	70.0
5.0	85.0
6.0	95.0
10.0	150.0

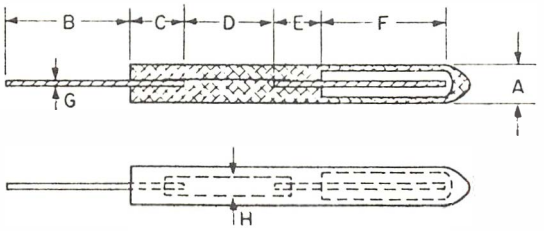


Figure 14.1.4
Dimensions of molybdenum seals (Table 14.1.4.1)

Table 14.1.4.1

Dimensions (mm) of MOLYBDENUM RIBBON SEALS IN QUARTZ (Figure 14.1.4)

Supplied by Thermal Syndicate

Rating	A	B	C	D	E	F	Molybdenum wire G	Molybdenum ribbon H
2-3A	4-5	25	8	12	8	25	0.3	1.5x0.0156
4A	5-6	25	10	14	10	25	0.45	2 x0.0156
6A	6-7	25	10	18	10	25	0.7	3 x0.0156
8A	7-8	25	11	18	11	25	1.0	4 x0.0156

The silica does not crack from stresses normal to the plane of the strip because of the small thickness of the metal. The metal must be thin enough to be stretched by tensile stresses insufficient to break the glass, yet not so thin that it is itself fractured. Molybdenum strip as thin as 0.01 mm is liable to be fractured by these tensile stresses if its width exceeds 2 mm, so that wider strip must be made with thicker material. The optimum thickness of the strip depends on the mechanical properties of the metal. Low yield stress and high ductility are obviously desirable, but the metal must not be so weak that fracture occurs.

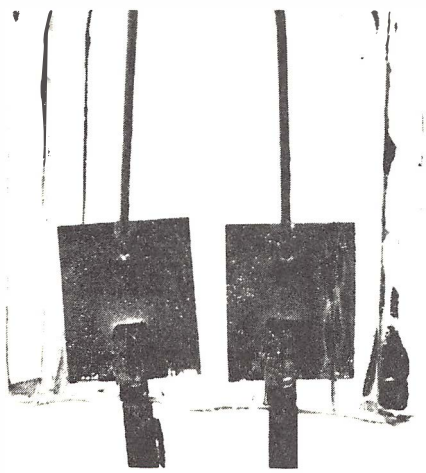


Figure 1
Press seal-T-8 tungsten halogen lamp

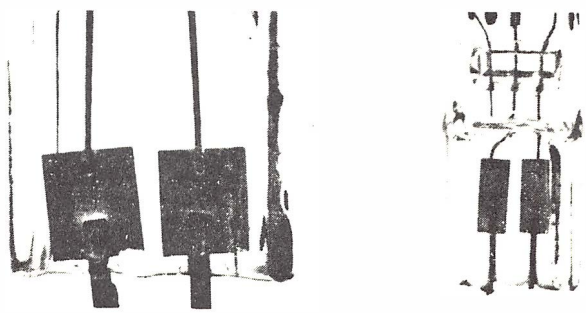


Figure 2
Press seal-T-4 single-end tungsten halogen lamp

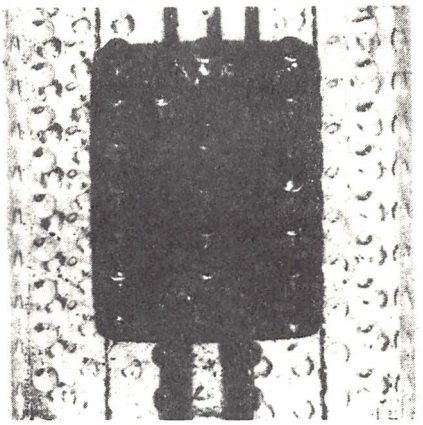


Figure 3 Twenty-ampere press seal.

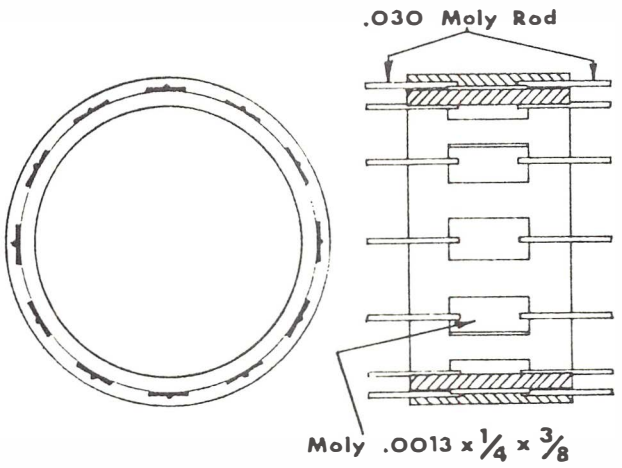
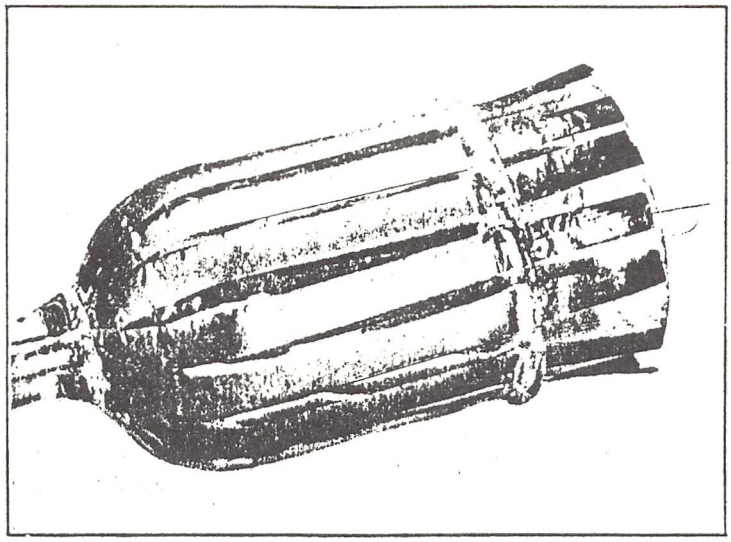


Figure 4 Circular seals

Since the cross section of the ribbon is limited, for heavy currents a number of ribbons may be connected in parallel, disposed in a circle around a silica rod or tube contained within a larger tube. The outer tube is then collapsed so as to seal the ribbons between the inner and outer silica.



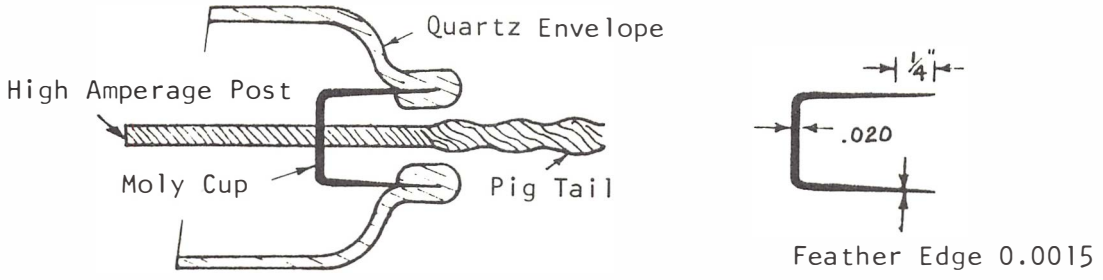
Molygdenum Ribbon - Silica Seal of the Concentric Type

The molybdenum ribbons are fused between two concentric silica tubes by collapsing the outer tube on to the inner with the ribbons in place.

14.2 TUBULAR MOLY TO QUARTZ SEALS

The limitations of current carrying capacity of moly ribbon seals can be overcome by use of the tubular moly to quartz seal.

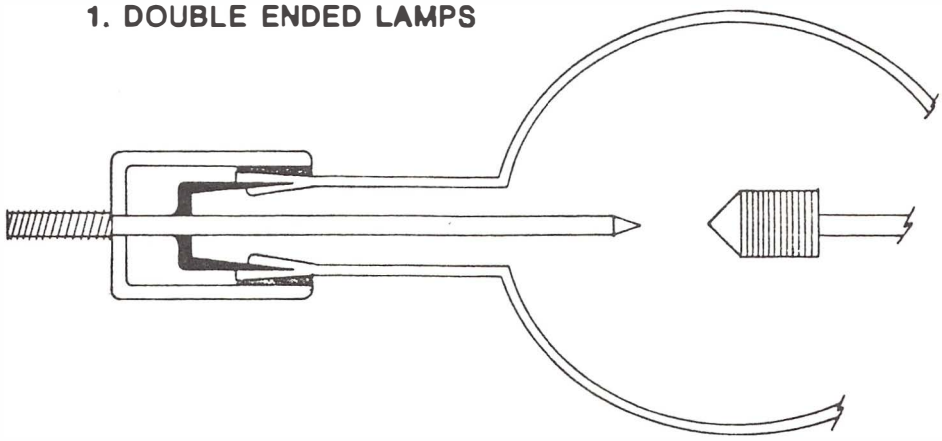
In concept it has long been possible to get around the current barrier imposed by ribbon seals by using a Housekeeper seal which removes the glass/metal interface from the circuit by using a feather edged cup. The heavy current conductor is coincident with the cup axis of symmetry and is brazed or welded to the cup. The open end of the cup has a feather edge to which the seal is made.



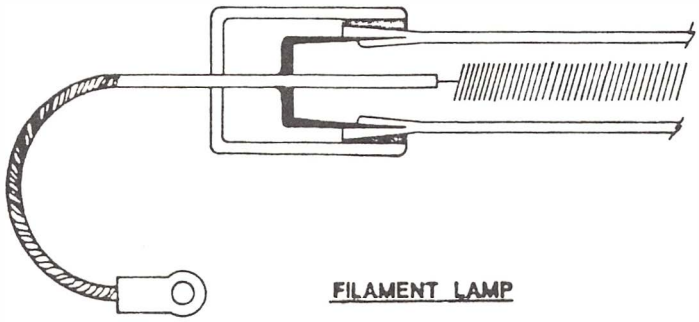
One Form of High Current Moly-Quartz
Seal Subassembly

-APPLICATIONS-

1. DOUBLE ENDED LAMPS

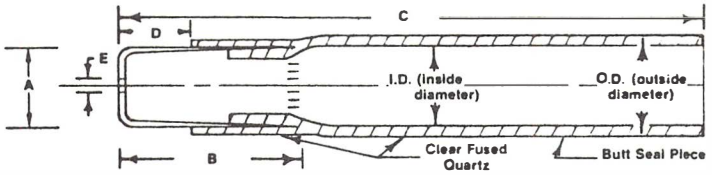


DISCHARGE LAMP

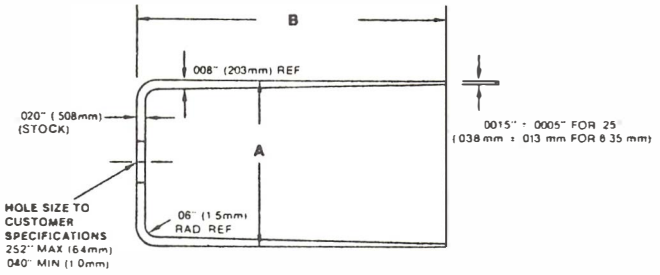


FILAMENT LAMP

Standard Moly-Quartz Seals



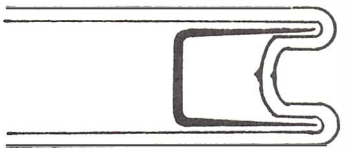
Molybdenum Feather Edged Seal Element



Bomco Part Number	A Moly Cup Size	B Cup Length	C Overall Length	D Cup Exposure	E Hole Diameter min.040"(1.0mm)	Quartz Size I.D./O.D.*
B2710S	.250" 6.35 mm	.500" 12.7mm	63mm	6 mm	.078" 2.0 mm Max	7/9 mm ±.5 mm
B2711S	.3125" 7.94 mm	.625" 15.88 mm	63 mm	6 mm	.078" 2.0 mm Max	8/10 mm ± .5 mm
B2692S	.375" 9.53 mm	.500" 12.7 mm	65 mm	6 mm	.125" 3.17 mm Max	10/12/mm ± .5 mm
B3523S	.500" 12.7 mm	.970" 24.61 mm	73 mm	8 mm	.250" 6.4 mm Max	15/18 mm ± .8 mm
B2694S	.625" 15.88 mm	.970" 24.61 mm	73 mm	8mm	.253" 6.4 mm Max	15/18 mm ± .8 mm
B2712S	.750" 19.05 mm	.970" 24.61 mm	90 mm	8 mm	.253" 6.4 mm Max	17/19 mm ± .8 mm
B2670S	1.00" 25.4 mm	.970" 24.61 mm	100 mm	8 mm	.253" 6.4 mm Max	22/25 mm ± 1.0 mm
B3572S	1.250" 31.75 mm	.970 24.61 mm	100 mm	10 mm	.253 6.4 mm Max	30/33 mm ± 1.2 mm
B2610S	1.500" 38.11	.970" 24.61	100 mm	10 mm	.253" 6.4 mm Max	35/38 mm ± 1.5 mm
B3377S	1.750" 44.45 mm	.970" 24.61 mm	120 mm	10 mm	.253" 6.4 mm Max	42/45 mm ± 1.8 mm
B2335S	2.00" 50.8 mm	.970" 24.61 mm	120 mm	10 mm	.253" 6.4 mm Max	48/52 mm ± 2.0 mm

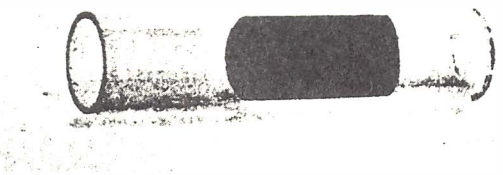
*Tolerance applies to quartz Outside Diameter

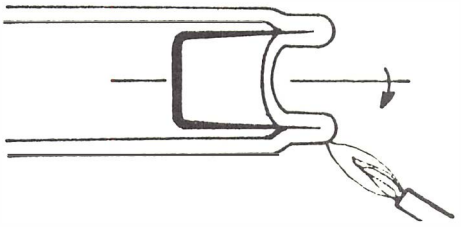
14.2.1



Step 1

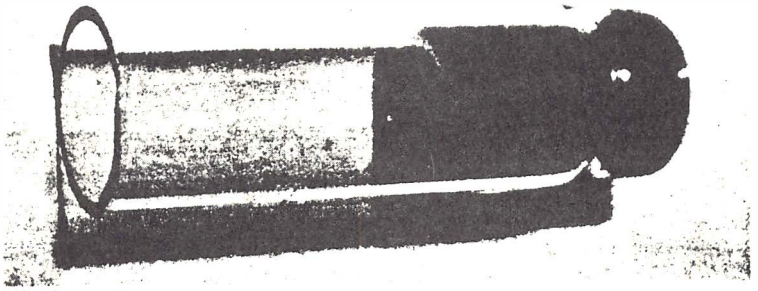
Clean and Assemble Cup & Vial

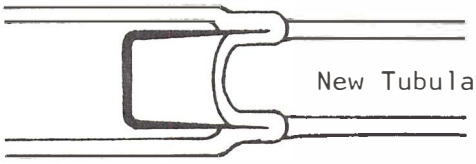




Step 2

Seal in Rotating Vacuum Chuck





New Tubulation Fused to Seal **Step 3**

Excess Quartz Removed **Step 4**

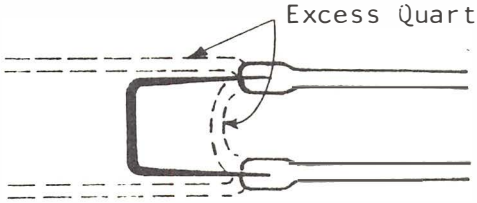
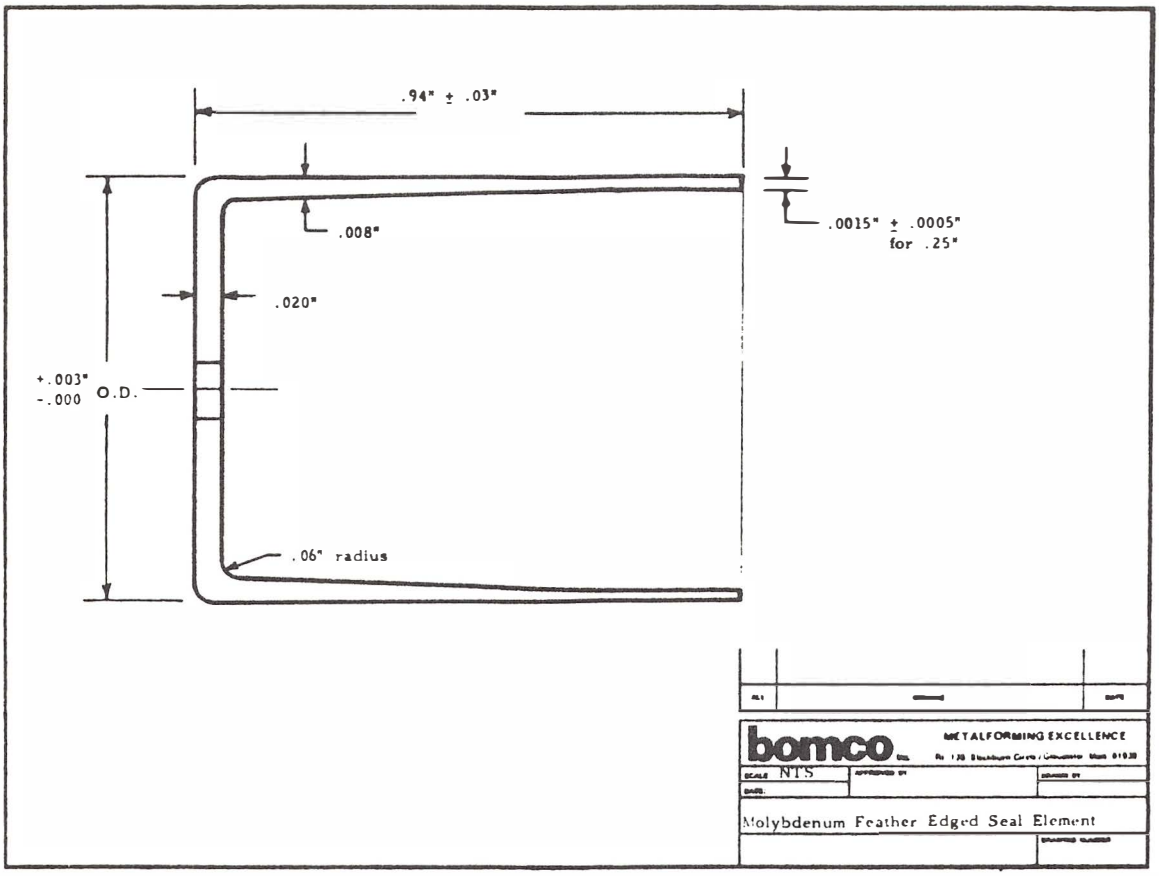


Figure 6. Moly-Quartz Seal Fabrication


.94" ± .03"
.008"
.020"
.0015" ± .0005"
for .25"
+.003"
-.000 O.D.
.06" radius
bomco
METALFORMING EXCELLENCE
SCALE NTS
Molybdenum Feather Edged Seal Element

Dec. 15, 1970 D. R. DAYTON ET AL 3,547,508

METHOD OF SEALING QUARTZ TO METAL

Original Filed Nov. 25, 1966 2 Sheets-Sheet 1

FIG. 1

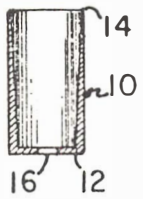


FIG. 2

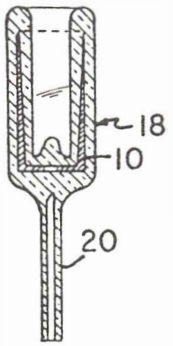
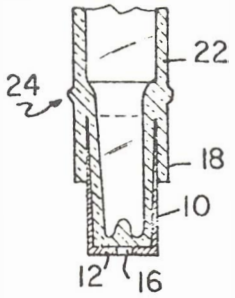


FIG. 3



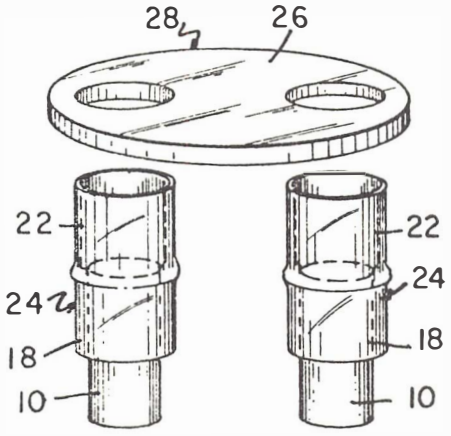


FIG. 4

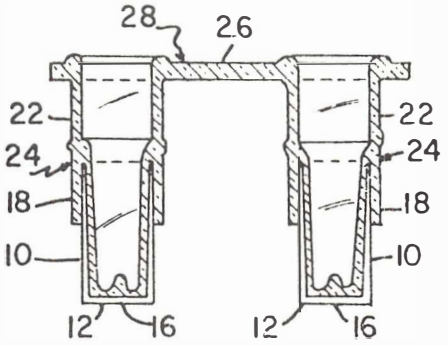


FIG. 5

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PAUL E. GATES
INVENTORS
BY Laurence Brown
ATTORNEY

Original Filed Nov. 25, 1966

2 Sheets-Sheet 2

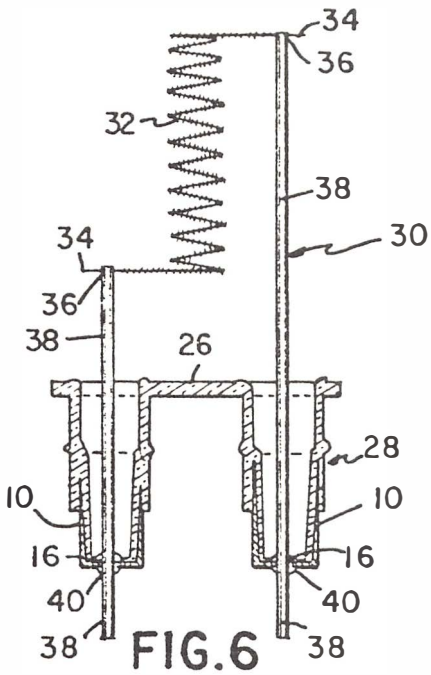


FIG.6

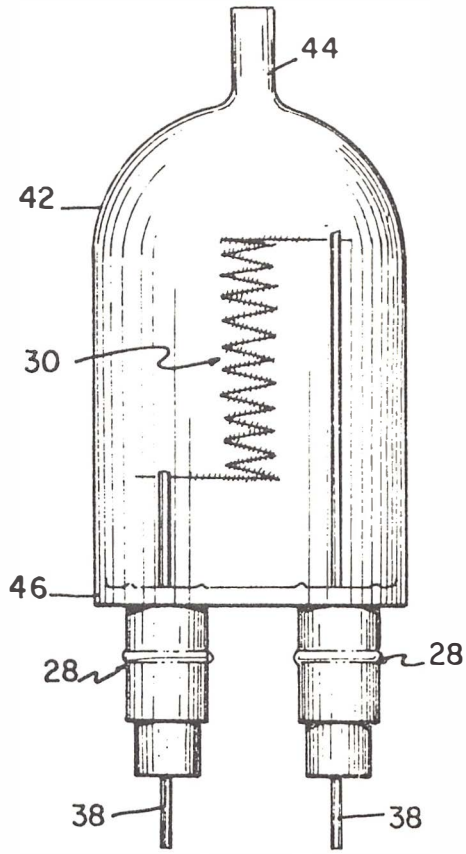


FIG.7

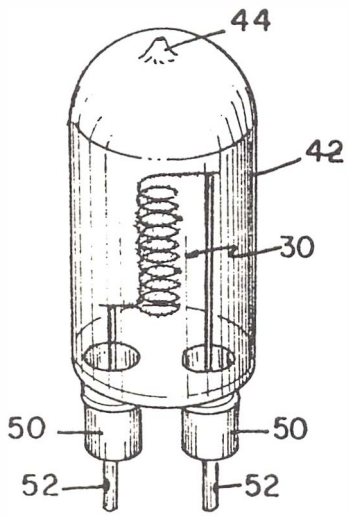


FIG.8

DAVID R. DAYTON
PAUL E. GATES
INVENTORS

BY [signature]
ATTORNEY

Patent #3,547,508 (cont)

The various figures of the drawings are the schematic view in the nature of a flow sheet depicting the various fabrication steps taken in our present invention.

In Figure 1 a tapered conductor cup is shown in cross-section showing in particular the taper and the centrally located hole.

Figure 2 shows the tapered conductor cup completely sealed in glass.

Figure 3 shows the encapsulated cup affixed to a glass tubular member showing the outer glass removed midway of the tapered cup.

Figure 4 shows two assemblies as described in Figure 3 in position to be affixed to a glass disc.

Figure 5 shows the completed assembly of the tapered cups and glass disc.

Figure 6 shows a filament assembly positioned and welded to the tapered cup.

Figure 7 shows a glass envelop sealed to the glass disc assembly with clamp legs fitted over the end wires and having an exhaust tube positioned for final sealing of lamp.

Figure 8 shows a complete lamp assembly.

In each of the figures of the drawing similar numerical designations are indicative of similar elements of structures.

In our present invention, we utilize a molybdenum cup as a sealing enclosure. In this way, the edges of the cup form a seal with a quartz envelope. The base of the cup is provided with a centrally located aperture for the provision of a filament-supporting conducting rod that is brazed or heli-arc welded in place. This provides an unrestricted current-carrying path to the filament of the lamp. With this novel arrangement, the problems encountered with current-carrying conductor seals are eliminated.

14.3 HARD GLASS TO MOLY SEALS

Moly to hard glass is a matched seal. That is the thermal expansion coef of the glass and moly wire are nearly the same. Moly can be sealed to several aluminosilicate and borosilicate glasses. For example: Corning types 7040, 7052, 7050, 7042, 7510, 8835, 1720, 1776, 7750, 7720, 7055, etc.

Unlike quartz to moly, for hard glass to moly seals, the moly must be oxidized. The bond is from hard glass to moly oxide and the bond of the oxide to the base moly metal. A seal with bright unoxidized moly wire will leak. Tungsten sealing and moly sealing are quite similar.

Tungsten and molybdenum are substantially pure, hard, brittle metals and are the only pure metals capable of being sealed directly to the low-expansion heat-resisting (or hard) glasses. They are difficult to work so that care must be taken to avoid splitting, both in fabricating into rod and wire and in cutting the finished material into the short lengths needed for seal making. Short lengths should be severed by grinding, during which chattering should be avoided, and not by mechanical cutters. Split wires are frequently recognized by a line seen during the process of coating them with glass, and the course of the crack is often revealed by a line of bubbles in the finished seal, as shown in Figure 14.3.1.

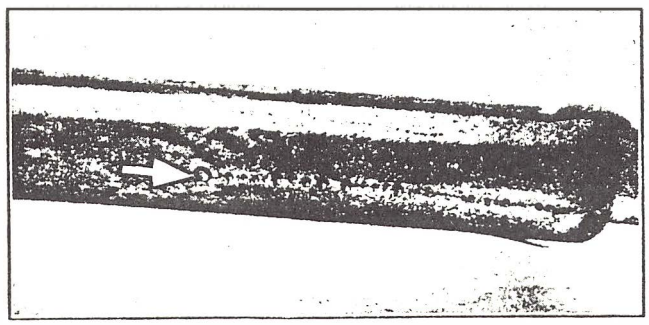


Figure 14.3.1
Crack in Tungsten Revealed by Line of Bubbles during "Glassing" Operation

Tungsten and Molybdenum are oxidized readily at comparatively low temperatures. Moly rapidly becomes coated with a thick non-adherent film of oxide. The degree of oxidization can be controlled by temperature or sealing in an inert atmosphere. Since relatively high temperatures are required for sealing, the only real world answer is atmosphere control. For sealing moly wires to a tube, the moly wires are preoxidized in a flame (to oxidize the seal area only). During sealing, the glass tube is flushed with nitrogen. The seal is thus made in an inert atmosphere. Care must be taken that the gas/oxygen flames

do not go under the open end of the tube and oxidize the moly by the entrance of combustion gases. Seals with good control of oxidation can be obtained by the flushing process. When the flushing process is not feasible, the wire is generally prebeaded in the seal area. This process requires fusing a tight fitting bead to the moly. The seal is started at one end and worked towards the other end so as to push the air out from the space between the glass and metal.

Molybdenum should initially be oxidized only to a slight yellowish or at maximum to a blue-green color.

To prevent "boiling" of the glass and excessive oxidation of molybdenum, Kohl recommends that the combustible gas should be bubbled through a 5 percent solution of boric acid in methyl alcohol or to pass the gas (or a part of it) through ethyl orthosilicate.

14.4 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

1. Vacuum Sealing Techniques, by A. Roth, Pergamon Press.

2. Glass to Metal Seals, by J. H. Partridge
   Published by The Society of Glass Technology
   Hallan Gate Road, Sheffield, England.

3. Quartz to Metal Seal - U.S. Patent #3,320,352, General Electric 1967.

4. Method of Making a Moly-Tungsten Thimble Seal
   U.S. Patent #3,435,180 - General Electric 1969.

5. Quartz-Metal Seal, U.S. Patent #2,504,522, General Electric 1950.

6. Quartz to Metal Seal Manufacture, U.S. Patent #3,634,056, General Electric 1972.

7. Method of Making Quartz to Metal Seals, U.S. Patent #2,659,964 General Electric 1953.

8. Method of Sealing Quartz to Metal, U.S. Patent #3,547,508 GTE Sylvania, D.R. Dayton, 1970.

9. Quartz Halogen Lamps - Two Kw and Up - by D.R. Dayton
   IES Journal - Vol. LXII, No. 4, April 1968.

10. Development of Tubular Moly-Quartz Seals for High Output Lamps by N.K. Banks, Bomco Inc., Gloucester, Mass. 01930 February 1974.

11. Ribbon Lead Construction, U.S. Patent #2,667,595 General Electric 1954.

12. Lead in Conductor for electrical Devices, U.S. Patent #3,621,111 General Electric 1971.

13. Handbook on Incandescent Lamp Design and Manufacturing by David R. Dayton, GTE Sylvania, Chapter 8, Section 8.9, (1979)

See Section on Press Sealing and Section on Outer Lead Oxidation Prevention for Further References Regarding Glass to Metal Seals.

15.0 GLASS TUBING CUTTING

There are several methods of cutting quartz or Vycor tubing. Some are faster than others, some are cleaner than others.

15.1 SCORE AND BREAK

The tubing is scratched with a diamond or carbide blade and then the scratched area is subjected to a tension stress by bending the tubing. The tubing will fracture at the score. The process is clean, but slow. The break is not precise nor necessarily square to the tubing. This process is best suited to small tubing like exhaust tubes.

15.2 DIAMOND SAW CUTTING QUARTZ AND VYCOR

There are two types of diamond saw cutting of quartz tubing: Dry Cutting and Wet Cutting. Wet cutting results in a smoother cut with less chipping.

The choice of dry or wet cutting is determined by the quality of the quartz tubing and/or the application of the quartz tubing. Quartz and Vycor tubing with little or no air lines can be wet cut. Tubing for halogen lamps is usually wet cut. Commercial grade quartz (some air lines) for mercury lamps is usually dry cut because water will enter the air lines during cutting. When the quartz is heated for press sealing or baked to reduce the Beta value, the water in the air lines converts to steam and often cracks the quartz or blows out at the air lines. Removal of the water from the air lines by cold vacuum or a long bake at a little over 100°C would allow wet cutting of commercial grade quartz for mercury arc tubes.

15.2.1 Dry Diamond Saw Cutting

The dry quartz cutting process is as follows:
The basic machine consists of a motor and spindle fixed to a table. The spindle must run true so that there will be no wabble in the saw blade. The quartz tube is held in a fixture by hand. The fixture rests on bearings such that the quartz tubing can be pushed into the circular saw blade. A typical diamond saw blade is 6" in diameter and 1/32 " thick. The diamonds (man made) are imbedded in resin at the outer periphery of the blade. The shape of the resin-diamond form is tapered such that

only the extreme outer surface is in contact with the quartz. The surface speed of the blade is approximately 10,000 feet per minute. In the case of the 6" saw, the rotational speed is 6200 rpm.

Standard Commercial Diamond Saw Blades are available from:

Magwen Diamond Prod. Inc.
P.O. Box 3276
Framingham, Massachusetts, USA
01701

6" x 1/32" x 3/4" Bore

#CMD 220 x 550

Parson's Diamond Ent., Inc.
9 Lordship Road
East Granby, Connecticut, USA
06026

Bay State Abrasives
15 Union Street
Westboro, Massachusetts, USA
01531

The saw blades are available in 180 or 220 grit. The 180 grit will cut faster and more rough. The 220 grit gives a smoother cut with less chipping.

The diamond saw needs to be dressed occasionally to renew the diamond surface. The need is evident by reduced cutting speed and more rough cut and chipping. What hapens is the resin covers a percentage of the diamonds and acts like a saw without teeth.

Wheel dressing is accomplished by pressing a white or black dressing stick against the saw blade. The choice of the white or black dressing stick or a combination of both is an experience factor or trial and error.

Dressing sticks are available from:

Chander and Farquhar
900 Commonwealth Avenue
Boston, Massachusetts, USA
02215

Black Dressing Stick 37-C100-L7V

Parsons's Diamond Enterprises, Inc.
9 Lordship Road
East Granby, Connecticut, USA
06026

White Dressing Sticks

The life of the saw blade and the quality of the cut is operator technique. When the saw is about to break through the wall of the tubing, the feed must be slow to keep from breaking the thin section.

15.2.1.1 Operator Safety

The operator must be protected from the quartz dust as well as equipment malfunctions. For this reason, the entire saw is contained in a box with a suction fan to remove all silica dust as it is generated during the cutting process. The long pieces of tubing to be cut are also stored in the chamber for convenience of the operator. As the pieces are cut, they are placed in a polypropelene basket for washing, etc.

15.2.1.2 Quartz Tube Cleaning - Recommended Process

Quartz Tube Wash - Process Specifications

I. Equipment

A. PRERINSE TANK. Glass-lined steel. Overflow standpipe. Size 24" I.D. x 30" high. 60 gal. 24" liquid level (approx. 48 gal). Running tap water, approx. 1.5 gpm.

B. ACID TANKS (3). Polypropylene. Filled with equal volumes of acid (70% Nitric - 49% Hydrofluoric Mix) and Deionized Water.

- One tank is 27" x 15" x 14" deep 25 gal.
- Two tanks are 22" x 15" x 14" deep 20 gal.

C. PREFILTERED TAP WATER RINSE TANK. Polypropylene.
22" x 15" x 14" deep 20 gal.
Running Water, about 1.5 gpm.

D. FIRST DI WATER RINSE TANK. Polypropylene.
22" x 15" x 14" deep 20 gal.

E. SECOND DI WATER RINSE TANK. Polypropylene.
17" ID x 25" high 25 gal.

F. ACETONE TANKS (3). Polyethylene.
17" ID x 25" high 25 gal. Place inside steel cans.

G. DRYING CABINETS (3). Steel lockers, 3' W. x 1.5' D. x 6' high. 12" diameter openings in bottom (air inlet) and top (air outlet). Air pulled by acid exhaust blower. Inlet air filtered - 15' x 15' fiberglass filter over opening inside cabinet.

H. SINK. Acid resistant with exhaust hood.

I. PERFORATED POLYPROPYLENE BASKETS for carrying tubes. 11 1/2" ID x 12" high with handle. Side perforated with 1/8" holes, bottom with 1/4" holes.

J. COMPRESSED AIR GUN, 30 psi MAX.

K. HYDROMETER for Measuring Acetone Specific Gravity.

II. Materials

A. TAP (CITY) WATER.

B. NITRIC-HYDROFLUORIC ACID MIXTURE (SPEC. A-1)

C. FILTERED TAP WATER

D. DEIONIZED WATER (SPEC. A-2)

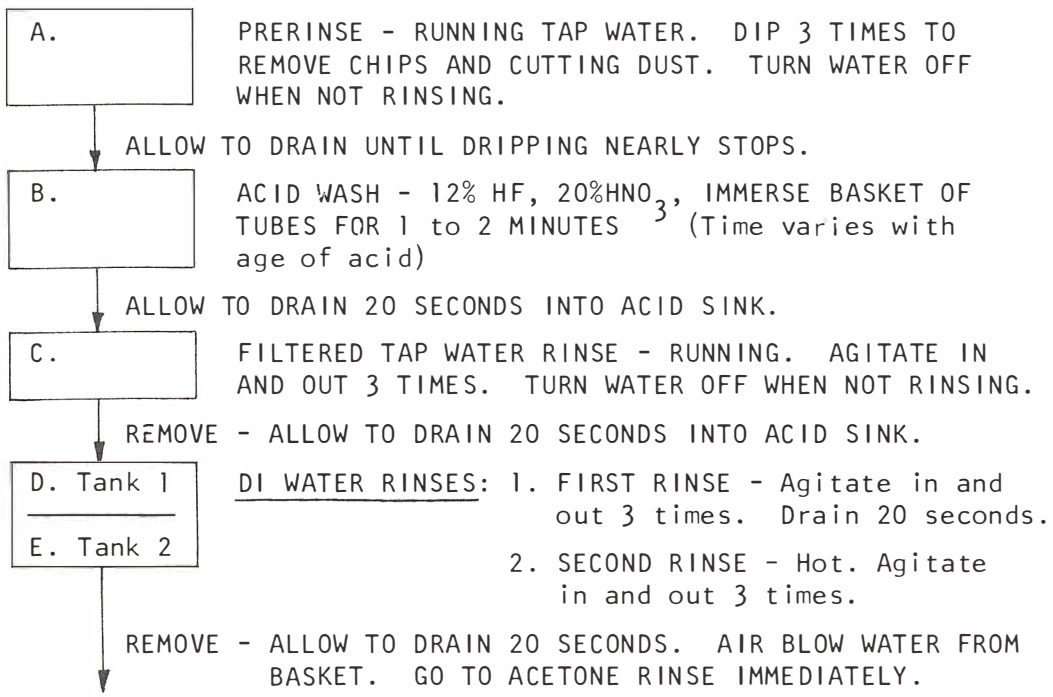
E. HOT DIONIZED WATER - 90 - 170°F.

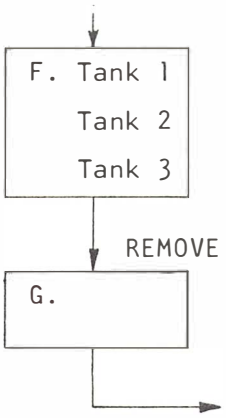
F. ACETONE - RECLAIM GRADE.

G. ACETONE - INDUSTRIAL GRADE (SPEC. A-3)

H. COMPRESSED AIR

III. PROCESS FLOW - BOXES SHOW LETTER IDENTIFYING EQUIPMENT DESCRIBED IN I.





ACETONE - 3 TANKS. AGITATE IN AND OUT 3 TIMES IN EACH TANK. TANK 1 FIRST (Reclaimed Acetone), TANK 2 SECOND (used acetone from Tank 3), TANK 3 LAST (New Acetone). ALLOW TO DRAIN FOR 10 SECONDS BETWEEN RINSES.

REMOVE - ALLOW TO DRAIN ABOUT 1 MINUTE.

DRY. PLACE BASKET OF TUBES IN DRYING CABINET UNTIL COMPLETELY DRY.

PLACE BASKET IN BAKING AREA.

IV. EQUIPMENT CLEANOUT, MAINTENANCE, MAKEUP

A. PRERINSE TANK. CLEANOUT BY OPENING TAP WATER VALVE 1/2 TURN FOR 10 MINUTES, ONCE PER SHIFT.

B. ACID TANKS. COMPLETELY CHANGE ACID SOLUTION EVERY 16 CUTTING-MACHINE SHIFTS (i.e., 4 machines, 2 shift schedule, will required a change every two days). REPLENISH LOSSES DUE TO CARRYOVER AND EVAPORATION WITH EQUAL VOLUMES OF ACID MIX AND DEIONIZED WATER.

C. FILTERED TAP WATER RINSE TANK.

1. CLEANOUT BY OPENING LINE TO FULL FLOW ONCE PER WEEK, OR SOONER, IF REQUIRED.

2. WATER FILTER - CHANGE ONCE PER MONTH.

D. DI WATER RINSE TANKS.

1. FIRST TANK - BRING UP TO FULL EVERY 3rd BASKET WITH SLIGHT OVERFLOW.

2. SECOND TANK - CHANGE TWO TIMES PER SHIFT (Hot DI water)

E. ACETONE TANKS, LIQUIDS

TANK 1 - USE RECLAIMED ACETONE ONLY. CHANGE DAILY.

TANKS 2 and 3 - CHECK SPECIFIC GRAVITY OF TANK 3 AT BEGINNING OF EACH SHIFT. WHEN SPECIFIC GRAVITY EXCEEDS 0.805, DO THE FOLLOWING:

1. DISCARD TANK 2 CONTENTS AND CLEAN OUT TANK.

2. MOVE TANK 3 TO TANK 2 LOCATION.

3. PUT FORMER TANK 2 IN TANK 3 LOCATION AND FILL ABOUT 1/2 FULL WITH NEW ACETONE (S.G. 0.795 to 0.800).

F. DRYING CABINETS

1. CHANGE AIR FILTERS MONTHLY.

2. VACUUM CLEAN INSIDE WEEKLY.

15.2.1.3 BETA CONTROL

For mercury lamps, the Beta value or Hydroxyl content (H + O + H) of the quartz must be low. The Beta value of the as drawn quartz is too high and is reduced by baking in air at 1050/1100°C for six hours. Vacuum baking is superior to air baking.

The Beta value is determined by dividing the absorbed radiation at 2.7 microns by the wall thickness in mm. For example, an as-drawn sample of quartz had an absorption value of .152 and a wall thickness of 2.62 mm.

$$\frac{0.152}{2.62} = .0580$$

The Beta value (B^{OH}) is .058 which roughly means that the water content of the quartz is 58 parts per million.

After baking in air at 1050°C for 6 hours, the same quartz had an absorption value of

$$\frac{0.009}{2.62} = .003$$

The new Beta value (B^{OH}) is .003 or the water content of the quartz is now 3ppm - a 94% reduction. The reduction would be even greater if the quartz was vacuum baked and back flushed with dry nitrogen.

15.2.1.4 INSPECTION

The completed cut pieces of tubing are 100% visually inspected for chips, wall thickness, length and general quality. During inspection, the bore of each piece of tubing is blown out to remove any dust accumulated during the air baking process and handling.

Note after acid wash, the quartz must be handled with clean gloves only. Finger prints will react chemically with the clean quartz and result in divitrification of the quartz.

15.2.1.5 SHIPPING

The quartz pieces are packed in compartmentized cardboard boxes for storage and shipping.

15.3 WET DIAMOND SAW CUTTING

The general process is as follows:

1. The quartz is drawn to four foot lengths and loaded into a polyproplene holder.
2. The quartz is acid washed with same acid solution of nitric acid and hydrofluoric acid as used in dry cut process. (See Section 15.2.1.2)
3. The acid wash is followed by two (2) tap water rinses and one (1) hot deionized water rinse.
4. The tubes are dried by forced air blowing through the tubes.
5. The tubes are then vacuum baked for three (3) hours at 1080°C to lower the Beta value. The bake time may vary depending on desired final Beta value. The Beta value is determined by measuring the absorption of 2.7 micron radiation. (See Section 15.2.1.3) The four foot lengths of quartz are now ready for cutting.

15.4 WET DIAMOND CUTTING EQUIPMENT

The quartz can be cut on same type of equipment as dry cutting by simply adding a continuous stream of water directed at the cutting area. However, the popular industry equipment is the Diamont Boart Co. Model DB-150 automatic multible cut machine. The number of tubes cut simultaneously depends on the tubing diameter. Fifteen or sixteen 10 mm tubes can be cut together. The saw blades are larger in diameter and thicker than dry cut blades. Typical dimensions of a wet saw blade are as follows:

Diameter	300 mm	(approx. 12")
Thickness	1.2 mm	(approx. 1/16")
Bore	16 mm	(approx 5/8")

The specific saw blade is selected for speed of cutting and quality of cut. The equipment can handle quartz from 5 mm to 25 mm diameter.

The cooling water is recycled until it becomes contaminated with quartz dust. Additives can be added to the water if necessary for better wetting.

The new diamond blade is correctly dressed, i.e., its surface shows a sufficient number of protruding diamonds for obtaining a good sawing result.

Should the release of the worn diamonds be too slow after a certain time of use, the disc cutting efficiency would diminish. The blade then is either clogged by material particles or becomes blunt. The disc is then said to be "glazed."

Dressing should be carried out with a special abrasive stone which should be applied against the impregnated diamonds with a moderate pressure.

Dressing should be performed as infrequently as possible in order not not to increase the wear of the blade

Slightly push the dressing stone towards the blade and make some cuts into the stone. Stop the cooling and the disc, and then check the condition of the cutting surface of the blade, by making a test cut.

15.4.1 Quartz Tube Cleaning - Recommended Process

After cutting, the pieces are loaded into polyproplene baskets for cleaning process. The acid wash process is the same as that used for dry cut quartz. (See Section 15.2.1.2)

15.4.2 Inspection

The quartz tubing sections are 100% visually inspected for length, wall thickness, chips and general quality. The quartz is packed in compartmentalized cardboard boxes for storage and shipment.

NOTE: During inspection the quartz must be handled with clean gloves. Finger prints would chemically attack the quartz and result in devitrification.

15.5 LASER CUTTING

The CO_2 Laser is an infrared focused beam with a wave length of 10.6μ. All types of glass and quartz absorb infrared energy at 10.6 microns at nearly 100% efficiency.

The method of cutting quartz with a CO_2 laser is direct evaporation of the quartz. It is not quite sublimation because glass is usually considered to be liquid of a high viscosity. The method of heating would be considered energy conversion. The laser is focused to a

very narrow spot on the outside periphery of the quartz tubing which is rotated 360°. The quartz is vaporized to a width approximately .005". There is a slight convergence of the beam which results in a slightly wider cut at the major diameter of the tubing and the narrowest cut at the inside diameter of the tubing.

The silica smoke is drawn away by a vent system. Usually a band of silica smoke deposits on the tubing very close to the cut. The cut piece is fire polished and results in a slight burr on the outside of the tubing. The fire polished edge results in a chip resistant cut such that coarse handling of the cut pieces is possible without chipping or nicking the cut tubing.

The experiments to date have been carried out with a 200 watt laser beam. The speed is approximately 36 in/min. of 0.50" thick quartz. Converted to 1" O.D. tubing, the speed would be approximately 10 pcs/min or 600/hr. Converted to T-3 the speed would be 1600 pcs/hr. of 0.50" wall thickness.

15.6 ELECTRON BEAM

Quartz has been cut by an electron beam at approximately same speeds as CO_2 laser cutting. The cut is by vaporization of a narrow band much like the CO_2 laser. The energy conversion mechanism is not clear and a curious difference in the cut is that the electron beam cut has a burr on the inside of the tubing where a laser cut has a burr on the outside of the tubing.

15.7 CUTTING HARD GLASSES

Hard glasses can be cut by the methods used for quartz and vycor, and in addition hard glass can be shock cut.

15.7.1 Heat and Score

This process is done on a high speed machine. The process is to heat a narrow band. The tubing is rotated in a very fine sharp gas/oxygen flame. The localized heat builds up a high tension stress on

the outside of the tubing. The highly stressed band is scored or scratched by a carbide blade. The glass is weakened and fractures at the stressed area. The cut end is then fire polished. The tubing is then indexed for the desired length of glass and cut again by the same method.

This process is best suited for glass lengths of one inch or longer and glass diameters in the 1/2" area. Small tubing is difficult to heat properly and large tubing is difficult to cut with a square cut without nickes or "finger nails."

15.7.2 Heat and Chill

The heat and chill process is similar to the heat and score except that a chilled or wet dull blade is brought into contact with the heated-stressed band on the tubing. The localized cooling increases the stress and the glass fractures. This system works best with higher expansion glasses but is used for some sizes of alumino-sililate glasses.

15.8 UNIVERSAL TUBING CUTTER ALL GLASSES

There has been some work done on a universal machine that will cut quartz, vycor, hard glass or soft glass at high speeds with a clean cut. The process is as follows: The tubing is fed through a compression head where the usual compression rubber had been replaced with an "O" ring. The compression head is tightened such that the "O" ring is trying to squeeze the tubing in a narrow area. This results in high localized tension stress perpendicular to the "O" ring. The tube is then scored with a diamond or carbide blade. The weakened score point generates a crack through and around the tube. The resulting cut is clean -- no silica dust -- and very sharp edged both inside and out. The sharp edges could be detrimental in some cases where it could cut rubber plugs or compression heads. The sharp edge could be fire polished for these applications. The work to date was done by Roger Parsons - GTE Sylvania Equipment Development, Ipswich, Massachusetts.

15.9 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

1. Quartz Manufacturing Plant - GTE Sylvania, Estes Street, Ipswich, Massachusetts 01938

2. Materials of High Vacuum Technology, by Espe, Volume II, Silicates, Pergamon Press - 1968

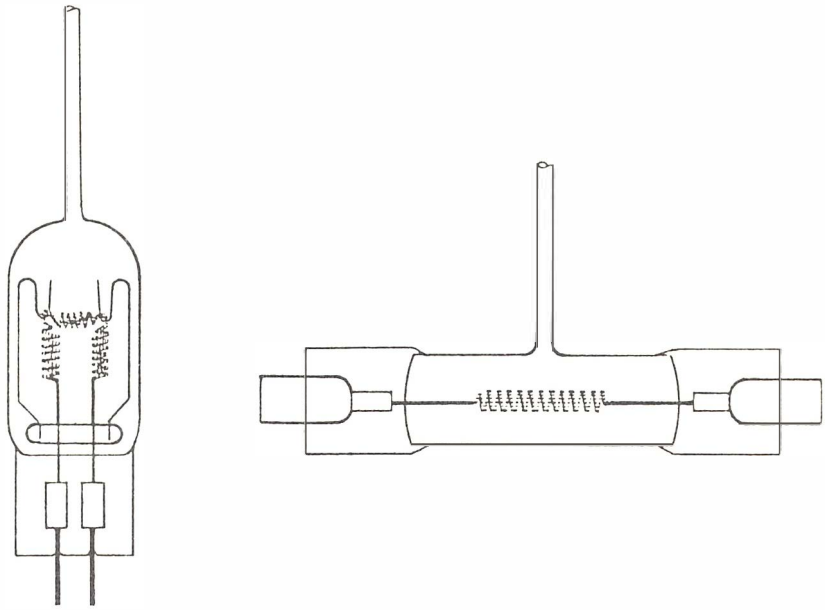
16.0 HALOGEN LAMP GLASS FABRICATION

16.1 TUBULATING OR STEMMING

There are basically two types of bulbs for halogen and discharge lamps:

1. Single End
2. Double End

The single end lamp has the exhaust tube attached to the dome of the bulb and the double end has the exhaust tube attached to the side of bulb tubing -- usually in the middle.



16.1.1 Single End Lamp

Single end lamp tubulating is a two-step operation. The process begins with a cut piece of tubing for the body and a pre-cut exhaust tube. The first process is to dome one end of the body glass. There are two common methods of doming.

16.1.1.1 Doming

A. Spinning In

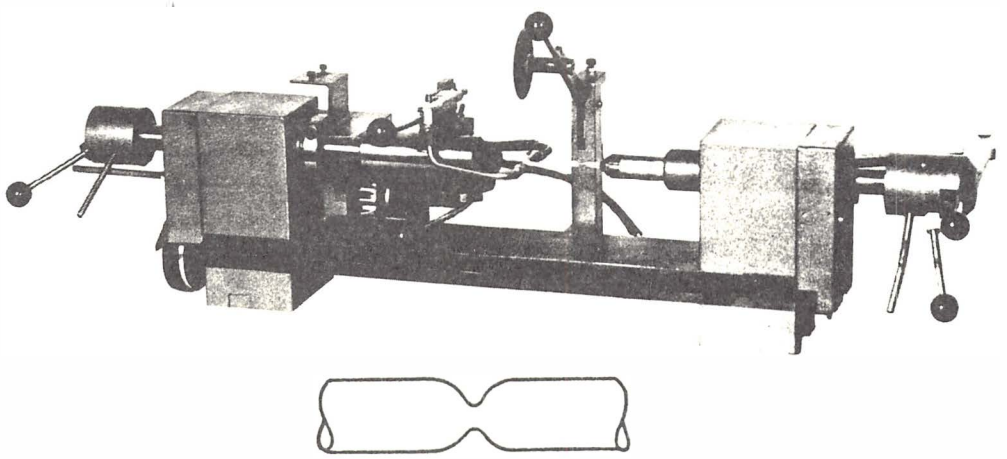
In the process, the tubing is held in a chuck and rotated at about 50 rpm. The end to be domed is heated by either gas - oxygen or hydrogen-oxygen flames. When the quartz or Vicor

has become plastic, a forming tool -- usually a contoured wheel -- is used to spin the end of the tubing towards the center and reduce the inside diameter to approximate that of the exhaust tube. This process is used for small tubing up to about T-6 (19 mm). The disadvantage to this method is the increase in wall thickness in the tubulation area. The glass in the original O.D. is compressed while the I.D. is reduced. The exhaust tube size is usually the same for a T-3 or for a T-6. Therefore, the bigger the bulb the more buildup of quartz thickness at the exhaust tube connection.

This process is done on automatic equipment at speeds of approximately 1500 per hour. Since the quartz is not heated any higher than necessary for forming, there is very little problem with silica smoke.

B. Restrict and Sever

In this process, the body glass is cut long enough to make two bulbs. This process will work for small diamater body glass, but is especially advantageous for larger sizes like T-7 or T-8 (25 mm). In this process, the tubing is held at each end and rotated. Gas-oxygen or hydrogen-oxygen flames are applied to the middle of the tubing. When the quartz has become plastic, a forming wheel (a copper disc about 2" in diameter) is pushed against the quartz to reduce the diameter as shown.



The forming wheel is adjusted such that the outside diameter in the reduced area is approximately the same as the exhaust tube. The quartz is highly stressed due to the forming and a slight bending movement will result in fracture at the neck. The result is two-domed bulbs.

The buildup of wall thickness is much less than with the spinning process because about the same amount of heated length is used to make two domed bulbs instead of one.

The process is done automatically at speeds of approximately 1000 per hour for T-8 tubing. The amount of heat energy needed for large size tubing is a problem because the entire machine gets heated. A new machine is being developed at GTE to use a plasma gun for final heating. This gun - a transferred Arc plasma gun - will result in a very high temperature in a localized area without heating the surrounding area.

C. Heat and Pull

There is a one-step process that is sometimes used for small body tubing sizes. This process is sometimes called nexing or restricting. The process can be done without rotating the tubing but is more uniform if rotated. Heat is applied by gas-oxygen or hydrogen-oxygen flames. When the quartz becomes plastic, the tubing is pulled axially a fixed amount. The amount of stretch and plastic condition of the tubing control reduction in outside diameter. This process is used for the hard glass halogen lamps.

16.1.1.2 EXHAUST TUBULATION

The exhaust tubulation is a butt seal. The process can be done while both parts are stationary, but is perhaps a little more controllable when both parts are rotating. The actual process is generally as follows:

a. The exhaust tube and domed bulb are lined up axially to each other. It is not mandatory, but the bulb is usually vertical and either dome up or dome down. The two parts are spaced about one inch apart.

b. The dome and end of exhaust tube are both heated. More heat on dome because the mass is larger.

c. As soon as the surface of the parts are "tacky," the parts are brought together.

d. Heat is applied to the joint.

e. As soon as the parts are fused, the exhaust tube is pushed down about 1/32" and them pulled up about 1/16". This action works the fused joint to eliminate reentrant angles and also reduces the inside diameter from approximately 2 mm to between 1 mm and 1 1/2mm. At the same time, the wall thickness is slightly reduced in the restricted area. The reduction in bore and wall thickness is helpful for tipping, especially for tipping lamps which contain frozen out gases. (Argon, Krypton or Xenon). Pumping is only slightly effected by a short restriction of 50-75% bore size. Below 50% reduction both pumping and filling will be effected.

16.1.1.3 Rotary Equipment

The complete process is done on rotary equipment automatically. The doming process is first and then butt sealed to the exhaust tube. Some equipment has a sizing die that comes up through the body glass and enters the exhaust tube connection to make sure that the hole is open and big enough.

The equipment for T-7 and T-8 is a walking beam for doming and a rotary for bulb sealing. The restrict and severing is done in the walking beam section and the resulting two domed bulbs are loaded

on the bulb sealing turret. On this machine, the bulb sealing will be done with the parts stationary. The stationary head will be simpler and less expensive to manufacture and maintain.

16.1.2 Double End

Mercury arc tubes and many halogen lamps are double ended and are tubulated in the middle. There are two standard processes for this operation.

1. Outside fire
2. Inside fire

16.1.2.1 Outside Fire

The lamp body glass is loaded in the jig which holds the glass tubing by both ends. The holders are also end seals. The tube is then pressurized and a sharp flame played on the desired tubulation point. Figure 16.1.2.1 shows the general sequence of events.

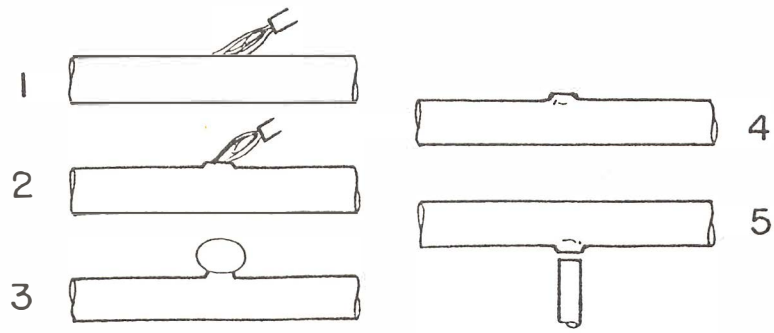


Figure 16.2.1.1

The butt seal is made essentially like the single end. In all cases, this seal is made with both parts stationary and again the short restriction is made to facilitate tipping.

16.1.2.2 Inside Fire

In this method a small burner is inserted into the body glass and heats the tubulation spot. The flame blows a hole in the body glass. After the hole is formed, the burner is removed and an outside fire used to make the butt seal as in the

outside fire method. The inside burner is usually hydrogen-oxygen. The outside fire method is usually preferred perhaps because there is usually a little less silica smoke left inside the body glass.

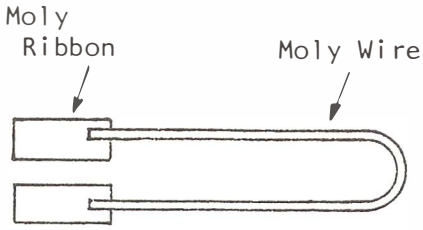
16.1.3 General Tubulation Data

The alignment of the exhaust tube to the body glass is critical for double-ended lamps. The exhaust tube must be perpendicular and normal to the lamp tubing. The operation following tubulation is press sealing. There will be considerable strain on the tubulation joint and breakage will occur if parts are not in good alignment. A good strong (good glasswork) tubulation is also required for best results.

Good alignment is also desirable for the single end, but it is not as critical as the double end. Concentricity is most important for single end lamps. Some press seal equipment has a position for heating the exhaust tube and realigning the lamp with respect to the exhaust tube.

17.0 MOUNT ASSEMBLY

The first step in mounting is to make the hairpin assembly.



This assembly is usually made on automatic equipment. The general cycle is as follows:

a. Feed moly wire, cut, form U shaped piece and transfer to head on indexing turret.

b. Feed 1st moly ribbon, weld to moly wire and cut ribbon to desired length.

c. Feed 2nd moly ribbon, weld to moly wire and cut moly ribbon to desired length.

NOTE: Depending on the type of "weld," the machine may feed a flux material to help make the moly-to-moly connection.

17.1 MOLY-TO-MOLY WELDING

There are several methods in use for attaching the moly leads to the moly ribbon.

17.1.1 Spot Weld - No Flux

Moly can be welded directly to moly under certain conditions.

a. H_2O cooled Tungsten electrodes in an argon atmosphere.

b. Tungsten (GE218CS) or (GTE NS-55) electrodes in Forming Gas (5%)

17.1.2 Spot Weld - Platinum Flux

This is really a Platinum braze. The Pt wets both pieces of moly. The platinum is used in several forms.

a. A Pt plated moly tab is inserted between the moly ribbon and moly lead. The actual connection is moly lead - Pt - moly - Pt - moly ribbon.

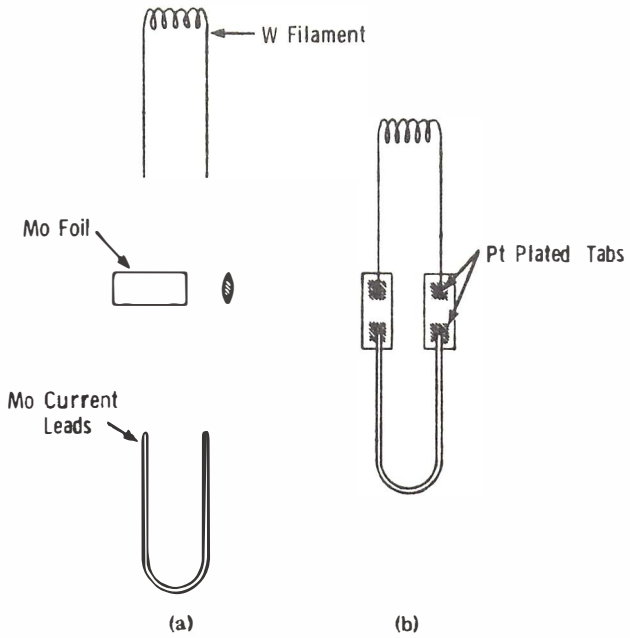


Figure 17.1.2.1
(a) Metal components
(b) Assembly of leadsets

b. One side of the moly sealing ribbon is Pt plated. The presence of a small film of Pt does not interfere with quartz to moly seal. The actual connection is moly lead to Pt to moly ribbon.

c. Platinum ribbon or wire is inserted between the moly ribbon and moly lead. The weld or braze only takes place in the area covered by the Pt.

NOTE: The Pt wire or ribbon must not extend beyond the margins of the moly ribbon or a defective seal will result.

17.1.3 Spot Weld - Tantalum Flux

A Tantalum ribbon or wire is inserted between the moly ribbon and moly lead. The weld or braze only takes place in the area covered by the Tantalum. The actual connection is moly - Ta - moly.

NOTE: The Ta wire or ribbon must not extend beyond the margins of the moly ribbon or a defective seal will result.

17.1.4 Spot Weld - Ta or Pt Paste Flux

Pt paste or Ta paste is dobbed on the moly ribbon and the moly lead wire placed on top of the paste. The weld is moly to (Pt or Ta) to moly.

The Pt paste is available from Engelhard Industries, 70 Wood Ave., Iselin, New Jersey 08830.
Number 6926 - Unfluxed Pt Paste.

17.2 MOUNT DESIGN FOR DOUBLE END LAMPS

The hairpin assembly for one end of a double end halogen or a mercury arc tube has only one lead. In this case, the hairpin assembly is made as shown if Figure 17.2.1.

Figure 17.2.1

17.3 COIL OR ELECTRODE MOUNTING

The termination of the coil can take several forms:

1. The leg of a single coil;
2. A slip-over coil on leg of single coil and heat crimped to leg of coil;
3. A coiled coil with an insert of tungsten wire. The primary coiling is heat crimped to the insert.

The completed mount for a single end halogen lamp has the general form shown in Figure 17.3.0.

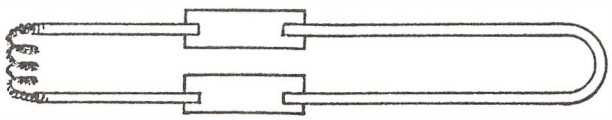


Figure 17.3.0
Halogen Lamp Mount

For long life (over 2000 hours) halogen lamps, the method of attaching the tungsten to the moly ribbon is critical. The best method is a direct weld W - Mo.

17.3.1 Spot Weld - Tantalum Flux

The weld is exposed to the halogen doped fill gas. In time, the halogen attacks the tantalum and converts the tantalum metal to a vaporized tantalum halide. When this occurs, the bond between the tungsten and moly ribbon is destroyed. Experimental lamps have been made in which the lamp failed because the inner lead essentially fell out of the press sealed joint. Microscopic examination showed a void where the Tantalum was originally. Lamps which had an "L" bend for welding to the moly ribbon kept the lead from falling out, but the current carrying connection was still poor.

17.3.2 Spot Weld - Platinum Flux

Platinum increases the rate of attack of bromine on tungsten by a 10 - 1 ratio. The use of heavy inner leads results in longer life for some lamps. The amount of Pt used to make the weld should be kept to a minimum. At press sealing temperatures, the Pt becomes molten and extrudes up along the inner lead and often projects into the actual lamp volume. The following SEM photographs show the attack of tungsten leads by bromine in the presence of Platinum.

Whatever the type of termination, the coil or electrode must be attached to the moly sealing ribbon. All of the methods used to attach moly to moly are used to attach tungsten to moly. However, the tungsten to moly weld must not only carry the same current as outer weld, but must also run hotter and is subject to attack by the halogen.

17.3.3 No Weld Flux Attachments

The best connection is tungsten to moly with no intermediate materials. Presently this is done in two ways.

17.3.3.1 Mercury Lamps

The electrode rod is slotted, the moly ribbon folded over once and inserted into slot in rod. The rod is then heat staked to capture the ribbon.

17.3.3.2 Halogen Lamps

There has been success with a double weld.

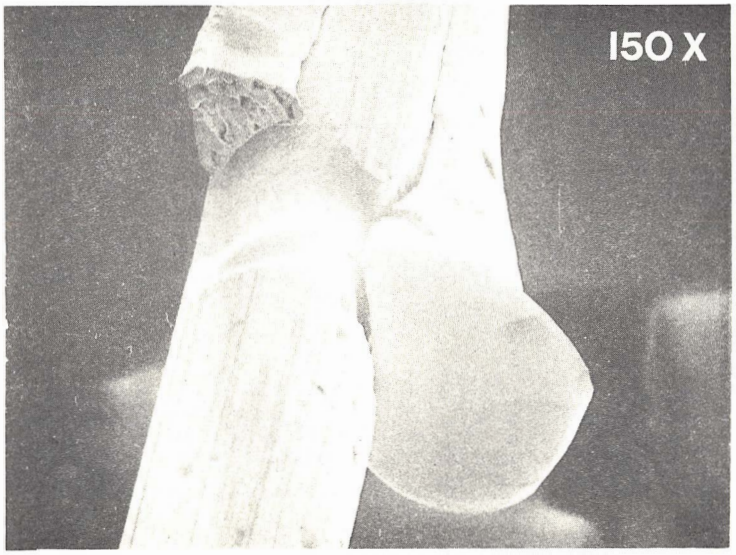
Double Weld, first weld is 80% of the second weld power. AC welders with cycle control. Welds are made under forming gas. First weld is not a weld but a cleaning action. Osram uses approximately two cycles (time) on each weld.

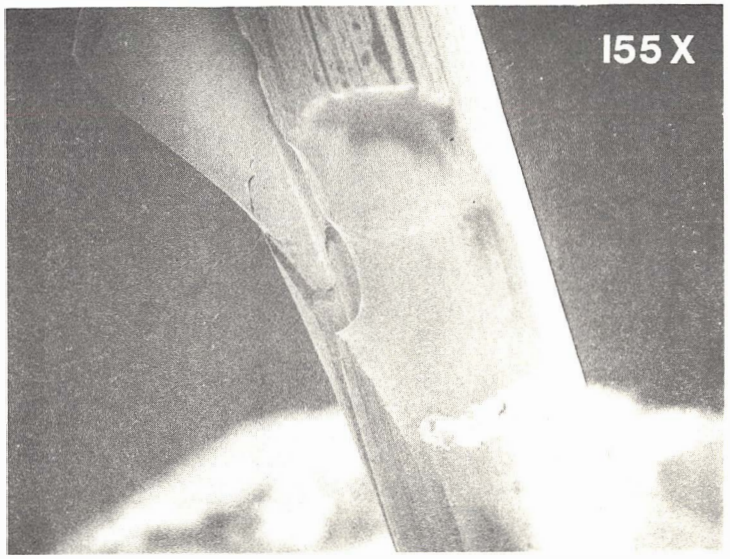
17.4 HEAT TREATING - FINISHED MOUNTS

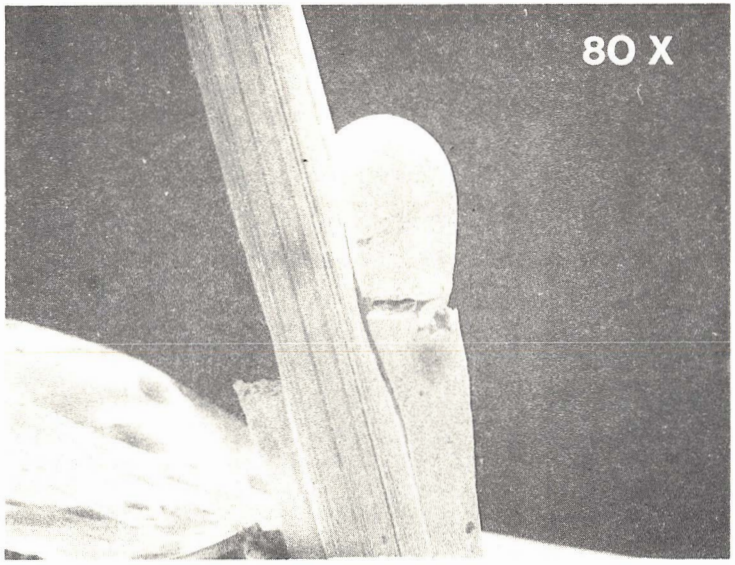
All mounts, just prior to sealing, should be heat treated at 1130°C for 10 minutes in dry hydrogen.

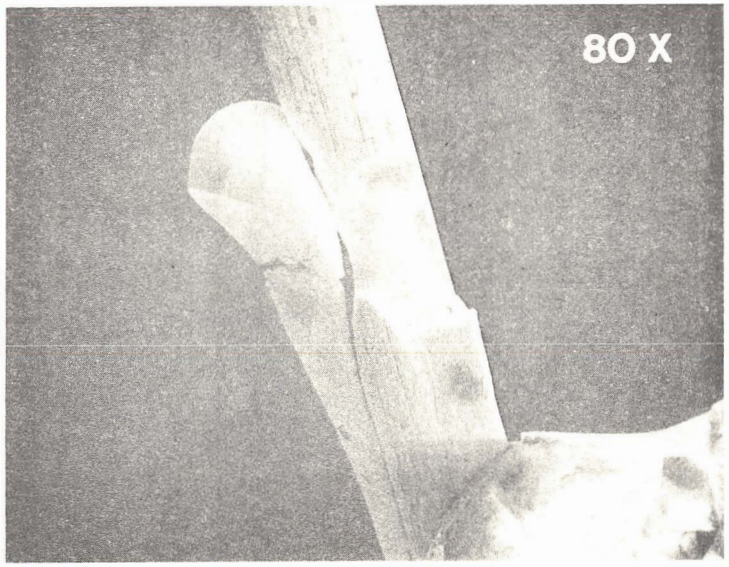
1500W/240V QUARTZ HALOGEN LAMP

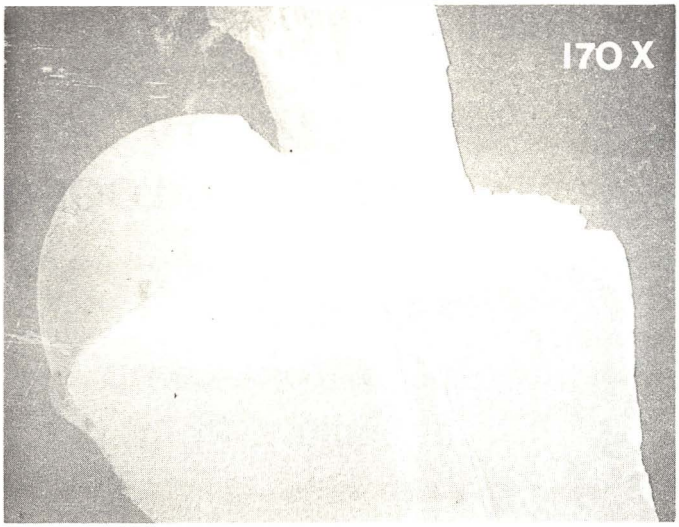
Platinum/Tungsten Interaction Area - Sample 1

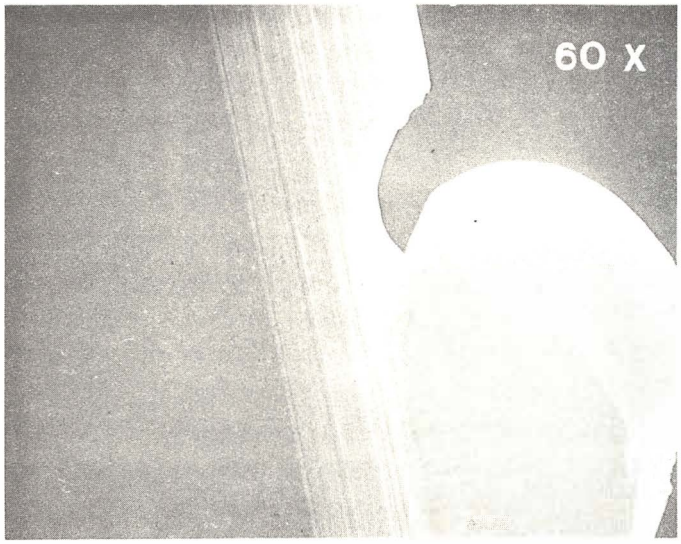


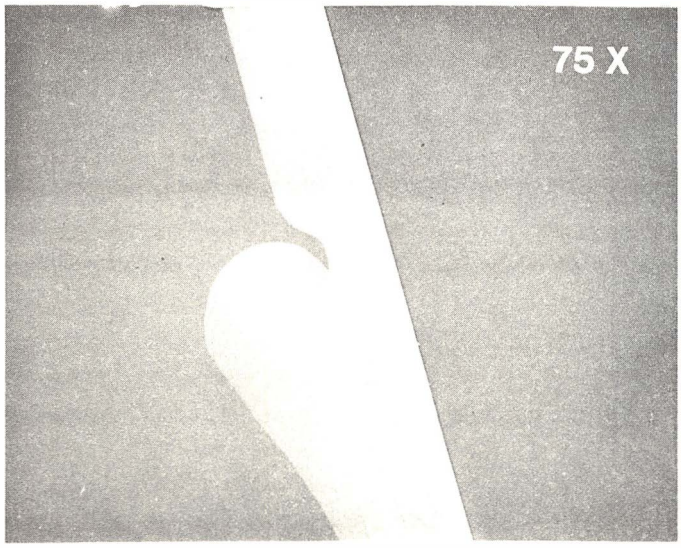






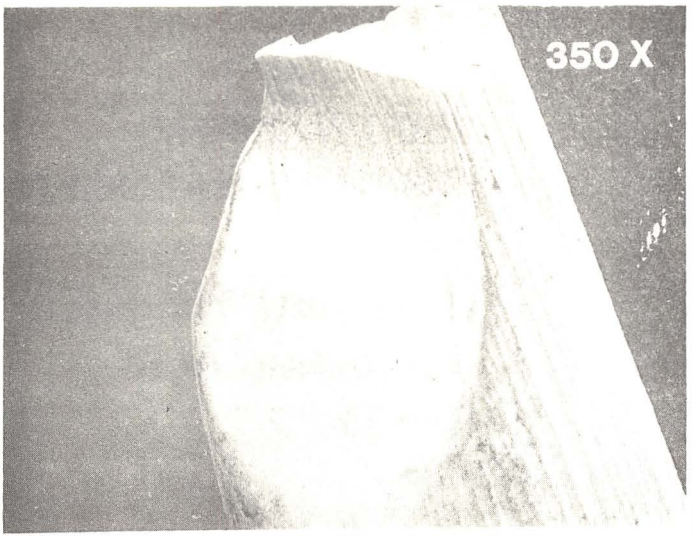


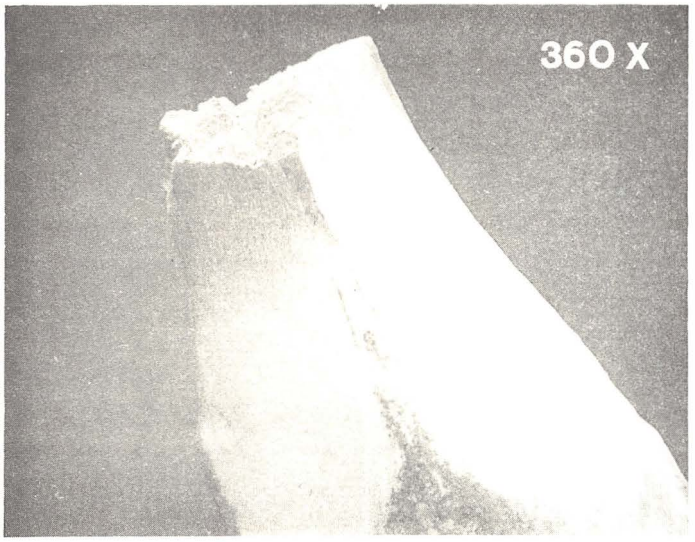


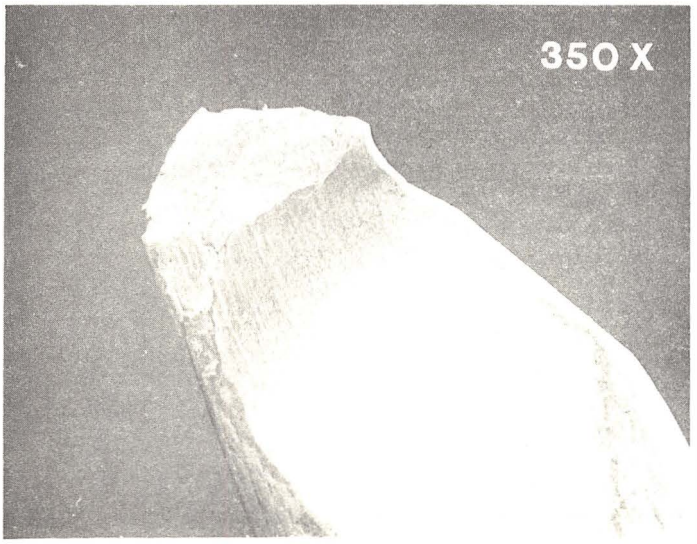


1500W/240 V
QUARTZ HALOGEN

Platinum/Tungsten
Interaction Area
Sample 2







1500W/240 V QUARTZ HALOGEN

Tungsten Wire from Lamp at Failure Point

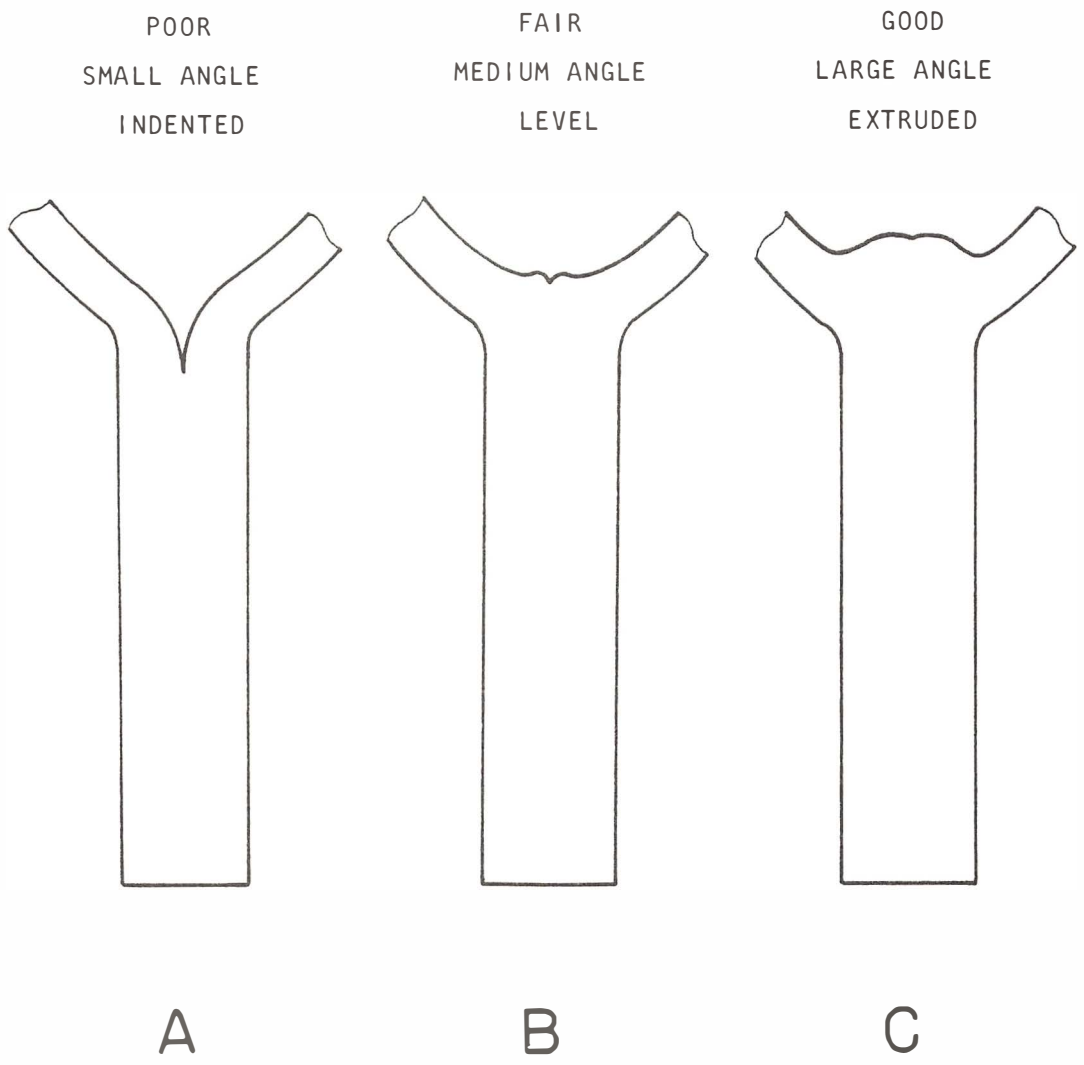

POOR
SMALL ANGLE
INDENTED
FAIR
MEDIUM ANGLE
LEVEL
GOOD
LARGE ANGLE
EXTRUDED
A
B
C

Figure 18.2.1

18.0 PRESS SEALING

Press sealing is the operation performed to hermatically seal the mount assembly to the body glass.

18.1 PRESS SHAPE

The shape and size of the press feet vary with different lamp types and quartz sizes. There are two general press types - the I Press and the Butterfly, or Flat, Press.

The I press is made with press feet which restrict the width of the press and allow the excess flow of quartz to fill a channel to form raised sections at the extreme width of press. The final shape is similar to a narrow flange I-beam,

The Flat press or "Butterfly" press has no restrictions and allows quartz to flow naturally. The flat press is probably a little more forgiving than the I press.

The I press is needed when bases are attached or minimum press dimensions are required.

The I press is more prone to split moly ribbon than the full press. This is because the restricted press is forced to extrude to a greater degree which puts more tension on the foil.

The following table shows pressing and inspection shrinkage of 1824, I-beam press seals and 2717 flat presses.

* PRESSING SHRINKAGE ANALYSIS

	I-BEAM	FLAT PRESS
SPLIT MOLY	108	4
DISTORTED BULB	4	
OXIDIZED COIL	13	2
SPREAD MOLY	2	
CLOSE MOLY	1	
BROKEN COIL	1	
HOLE IN BULB	2	
CROOKED COIL	1	
BROKEN EXHAUST	1	
CRACKED PRESS		3
NO MOUNT	2	
UNACCOUNTED FOR		20
TOTALS	135 (7.4%)	29 (1.1%)

** INSPECTION SHRINKAGE

	I-BEAM	FLAT PRESS
COLD PIPE	7	6
SPLIT MOLY	20	19
BUBBLED MOLY	8	2
BROKEN EXHAUST	4	6
CONTAMINATED COIL	6	2
BROKEN COIL LEG	2	1
BAD PRESS	1	2
TOTALS	48 (2.6%)	38 (1.4%)
NET GOOD	90%	98%

In addition, the time to set up an I press unit is about twice the time to set up for flat presses. The additional time is also reflected in set up shrinkage before production run.

18.2 PRESS STRENGTH

Most halogen lamps are filled to cold pressures above atmospheric and when hot, the internal pressure may reach 20 atmospheres (300 psi) or more. The geometry of the section where the press seal is exposed to the lamp body is the major factor controlling the burst pressure of the lamp. Figure 18.2.1 shows different configurations that result from pressing. (A) is the weakest. The reentrant angle is the start of the failure point. (B) is much more able to resist the tension forces and (C) is the strongest.

To achieve the desired press configuration requires extrusion of the quartz during press. The upward extrusion actually opens the reentrant angle and turns it inside out. This extrusion also tends to cause split molys by stretching them after being sealed to the quartz. The following is the test results of press jaw designs.

1. I-beam horizontal cross section and retangular vertical cross section (Figure 18.2.2A). Bulbs with this shape press area could not be made to withstand more than four atmospheres of pressure without tearing the foils. Using this press area, the foils remained parallel and crunching of the glass was not a problem.

2. Rectangular horizontal and vertical cross sections (Figure 18.2.2B) Bulbs tested with this shape press area had a slight crunching problem along the corners. Also, the foils tended to slant toward each other at the top. No problems of foil tearing or buckling were encountered when bulbs were made to operate filled with up to 16.7 atmospheres.

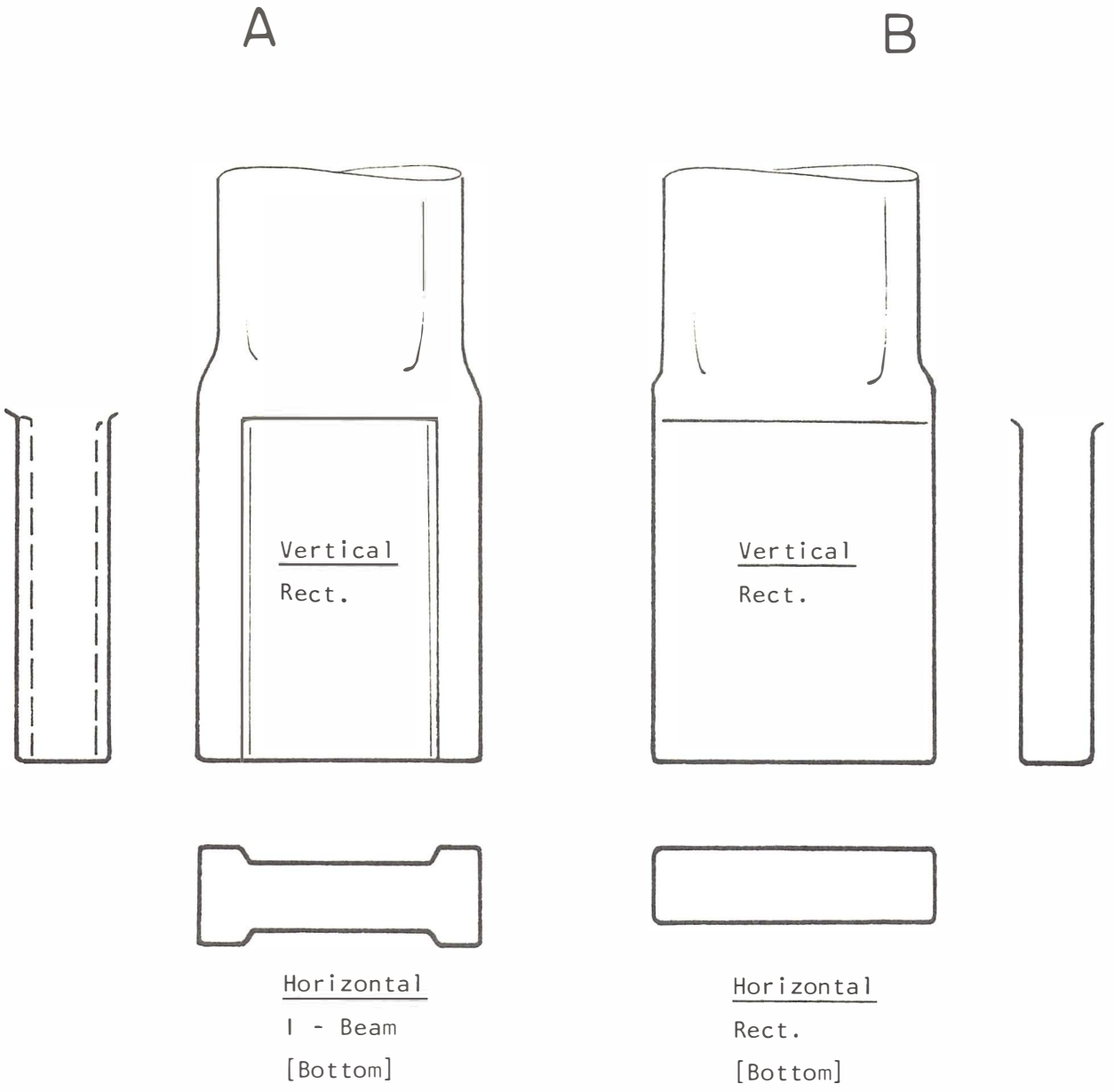


FIGURE 18.2.2 PRESS AREA SHAPE COMPARISON

3. Rectangular horizontal cross section and indented top vertical cross section (Fig. 18.2.2C) Bulbs tested with this shape press area had a crunching problem at the corners of the indented area and the foils were buckled and pulled in toward each other at their tops. This press shape did meet the six atmosphere pressure requirement. These press jaws were then altered slightly in order to produce rounded corners for the intendted area of the press (Figure 18.2.2D)

   This change of the press area reduced the amount of glass crunching somewhat, but the problems with the foils remained unchanged. Finally, these press jaws were machined to produce an I-Beam horizontal cross section about 50 percent as pronounced as that of the jaws originally used. These jaws produced a crunchless press area and a bulb that functions filled with 19.5 atmospheres of fill gas pressure at room temperature. However, the problems of the foils buckling and not remaining paralle! remained unchanged.

4. Retangular horizontal cross section and dual wedge vertical cross section -- when bulbs of this press area were made to function filled with six atmospheres of fill gas pressure, the press area corners were crunched. These jaws were changed to produce an I-Beam horizontal cross section similar to that used on the jaws described in (Figure 18.2.2E) The bulbs then produced would function when filled with 18.7 atmospheres of fill gas at room temperature.

   This press area shape did not produce a glass crunching problem. The foils remained parallel and were not buckled or torn.

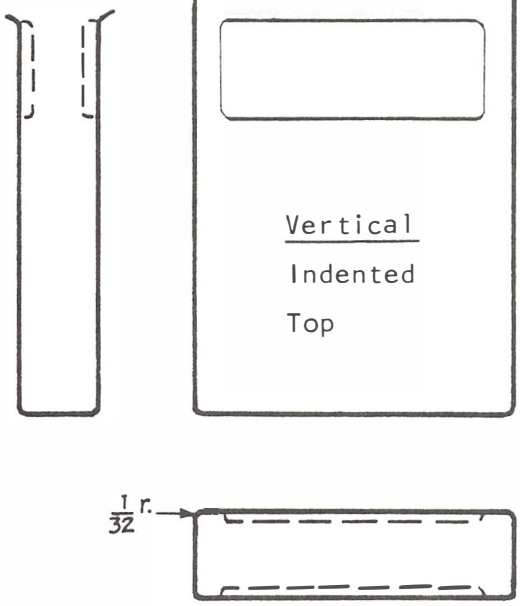
18.2.1 Moly Foil and Lead Size Effect on Press Strength

The data in following table shows both the smaller lead and the narrower moly foil help press seal strangth. This could be expected as the smaller the size of the foreign materials passing through the quartz, the stronger the press would be expected to be.

Lead	Moly	Avg. Bursting Point (P.S.I.)
.030"	.121"	776 ± 228
.040"	.121"	607 ± 188
.030"	.060"	1211 ± 300
.040"	.060"	1010 ± 362

One limit placed on this test was the maximum pressure on the pressure checking gauge was 1500 P.S.I. The limit was reached only by the narrow moly groups, with the .030" lead group having 36% over 1500 P.S.I and the .040" lead group having only 14% over 1500 P.S.I.

C



D

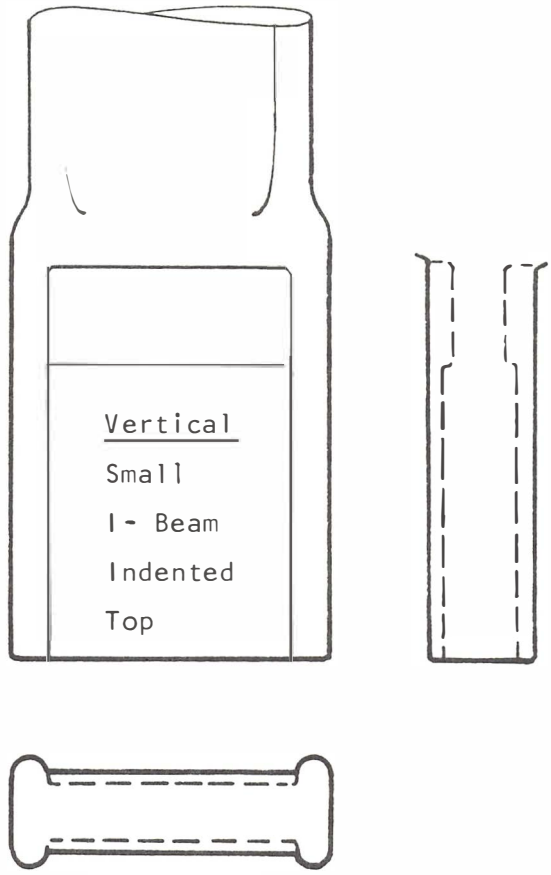
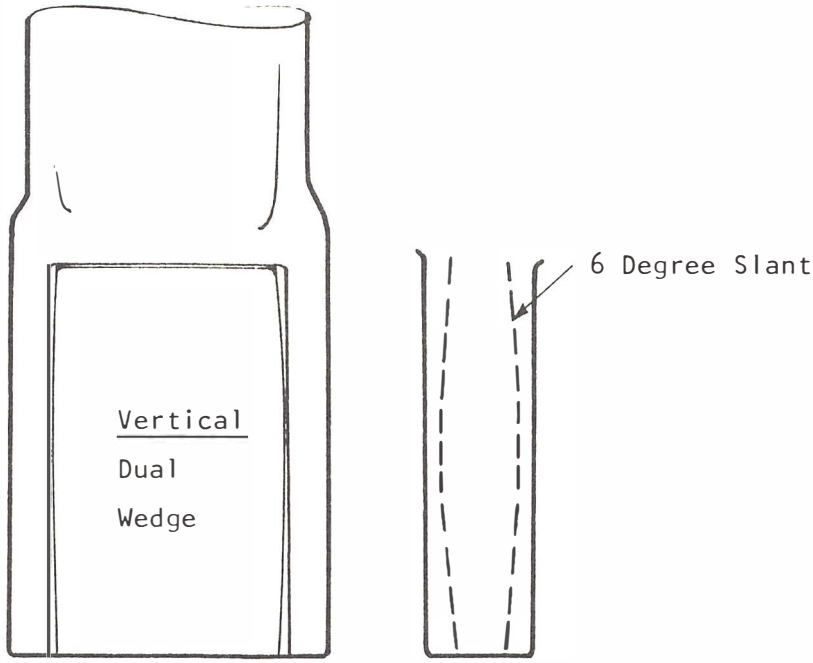


FIGURE 18.2.2 [CONTINUED]

E



Horizontal
Small I-Beam
[Bottom]

FIGURE 18.2.2.E [CONTINUED]

	PRESS SHAPE	PARALLEL FOILS?	TORN FOILS?	CRACKED GLASS?	BUCKLED FOILS?	FILL PRESSURE TOLERABLE (ATMOSPHERE)*
A.	I-Beam (Horizontal) Rectangular (Vertical)	Yes	Yes	No	No	4.0+
B.	Rectangular (Horizontal) Rectangular (Vertical)	No	No	Slight	No	16.5
C.	Rectangular (Horizontal) Indented Top (Vertical) (Rounded Corners)	No	No	Yes	Yes	6.0 - 8.0
D.	Small I-Beam (Horizontal) Indented Top (Vertical)	No	No	Slight	Yes	19.5
E.	Small I-Beam (Horizontal) Dual Wedge (Vertical)	Yes	No	No	No	18.7

Another factor in press strength is the amount of seal above the moly foils. There should be 1-2mm between the top of the press and the moly foils. Smaller leads, smaller coil legs and narrower moly foils all help in making a strong press.

18.3 OXIDIZATION PREVENTION DURING SEALING

The most difficult problem in the press seal operation is prevention of oxidization of the moly foil and also the filament. The basic solution is to protect the mount with an inert gas.

Double end lamps are pressed like two single end lamps. That is, one end is plugged while the other end is being heated and pressed. The exhaust tube is perpendicular to the plane of the press. In this type, the nitrogen flush gas enters the exhaust tube and is directed at side of lamp body. The gas loses its velocity, expands into the lamp body and flows out the open end before pressing. Provided that the flush gas is free of contamination and that the press seal fires are not located below the open end, there should be little or no mount oxidization with this type of lamp.

The most difficult lamp is a single end with a short, large diameter lamp body. With the single end lamp, the exhaust tube acts like a nozzle and directs the flush gas on to the mount assembly which breaks up the gas stream and then the gas somewhat unevenly and unpredictably flows out the end of the lamp. There have been several variations of flush gas set ups tried with varying degrees of success.

A. Insert needle through exhaust tube with hole in needle perpendicular to axis of exhaust tube. This makes the gas flow similar to a double ended lamp. This system has been successful, but is difficult to do on a production basis with different mount structures.

B. Double Flush. In this system some gas is flushed down via exhaust tube and some flushed up via holes in mount holder. This system has been somewhat successful for lamps which have the end of moly ribbon up higher in the lamp. The distance from end of lamp to end of moly ribbon varies from approximately 1/32" to approximately 1/4". This system does a good job of keeping the outer leads clean at entrance to the press. See Figure 18.13.1.

C. Up Flush. This system is used on tipless lamps. A needle is inserted up into the lamp from the bottom. The needle is part of the mount holder. The end of the needle is at least 1/8" above the end of the lamp during flushing. The needle is retracted just before pressing. This system is quite successful in tipless quartz IR lamps and is used to make automotive double end cartridge lamps (soft glass). To date, this system has only been used on single head press seals, possibly because when the head is not loaded, the needle will be directly in the fires. This problem can be overcome with programmable controllers, microprocessors, etc.

D. Combination Up Flush and Down Flush
This system would combine the standard exhaust tube down flush and the retractable needle up flush. The down flush could be used to flush out initial air before heating.

The up flush would eliminate any localized high velocity problems during heating and down flush would take care of loss of flush as needle was retracted and also be used for venting lamp pressure when press is complete or adding pressure to blow seal geometry after pressing.

18.3.1 Flush Gas Flow

The flush gas must keep mount from oxidizing. However, the flow must be kept low because the flow cools the inside of the body glass and will affect the quality of the seal as well as the time and economics of the system. The flush gas is usually nitrogen but can be Argon, Argon and nitrogen, or nitrogen and hydrogen (forming gas).

The forming gas acts to reduce the oxides on the mount during and after the press. The mount gets hotter right after the press when it is in direct contact with the quartz and the flow of flush gas has terminated. At this time, the oxides on the mount are reduced. The oxides on the mount parts enclosed in the seal may still be oxidized to varying degrees.

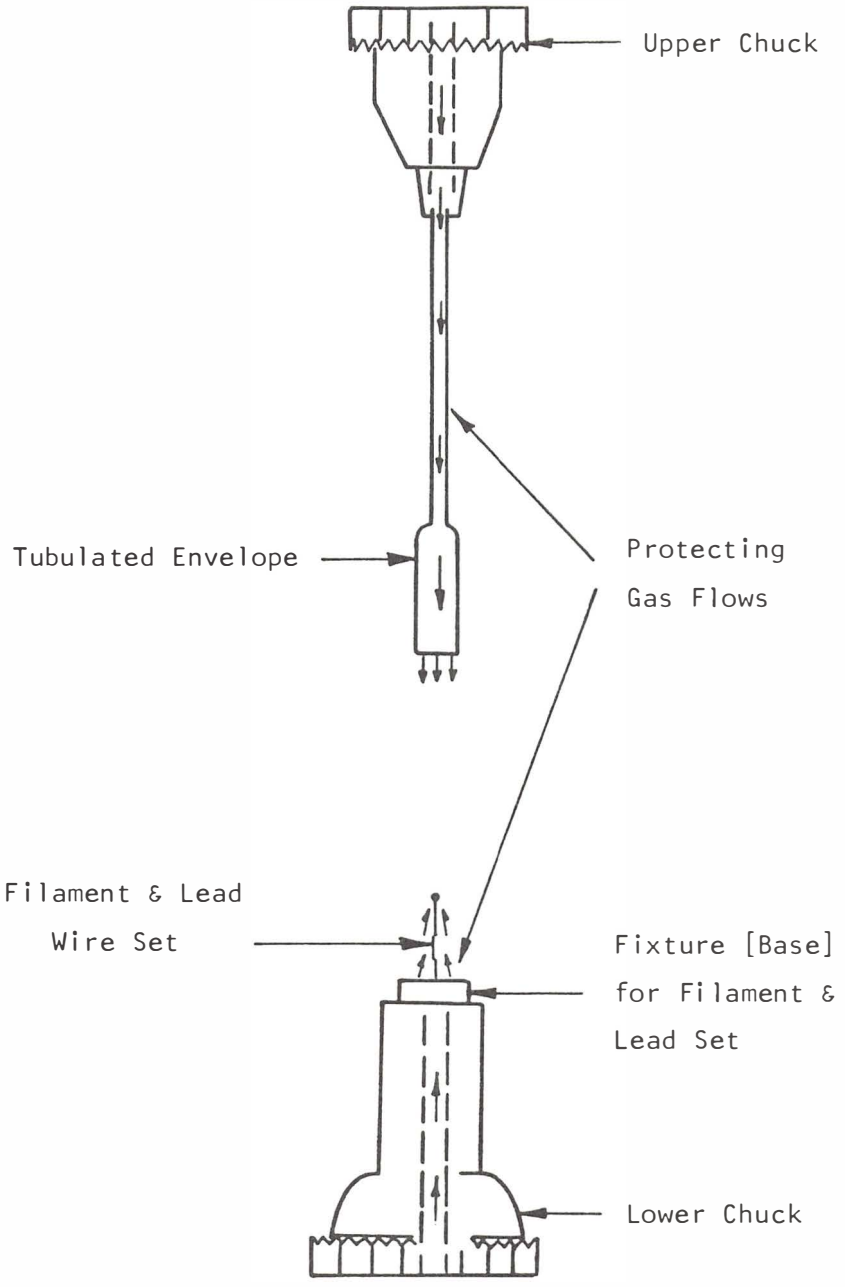
The following is a series of tests with the double flush system: One nitrogen stream flowed down through the exhaust tube, held in the upper chuck, and one flowed up through small holes in the filament fixture (or base) directed at the filament and lead wire set at a rate of 5 SCFH (Figure 18.3.1). Nitrogen was used as the protecting gas because of its inertness with respect to tungsten at standard pressure and 3000°F.

The adjustment of the heat of the burners at this time was such that if the flow rates of the nitrogen protecting gas were increased, the envelope could not be heated properly due to the cooling effect of the nitrogen.

After adjusting the flow settings and positions of the burners to their optimum conditions, several different means of filament protection were tested. An account of the gases and their flow rates tested and the results obtained are given below. This information is condensed in Table 18.3.2.

1. Nitrogen upper and lower flow protections of 15 SCFH and 8 SCFH, respectively -- No higher flow rates could be used without an undesirable cooling effect upon the quartz glass when heated. The filament and slip coils appeared clean after the press seal.
2. Argon upper and lower flow protections of 15 SCFH and 8 SCFH, respectively -- Argon was tested since it is much more dense gas than all the other protecting gases tested. This fact was expected to remove the possibility of turbulence with the air at the lower end of the envelope and thereby result in cleaner tungsten than the minimum standard after the press seal. The results, however, were the same as (1).
3. Seven to ten percent hydrogen in nitrogen upper flow of 1 to 15 SCFH and lower flow of 8 SCFH -- Hydrogen was mixed with the nitrogen as a reducing agent for any tungsten oxides formed on the tungsten during the press seal. This effort was made in order to achieve a tungsten cleanliness degree

FIGURE 18.3.1 TUNGSTEN PROTECTING GAS FLOWS



greater than the minimum standard. However, WO_3 was present on all filaments and slip coils tested. The oxidizing of the tungsten is believed to be due to the turbulence effect of the mixture tested with air in the envelope since this mixture was less dense than air.

4. Seven to ten percent hydrogen in argon, 1 to 15 SCFH upper flows and 8 SCFH lower flow -- Argon was used again in an attempt to eliminate turbulence with air in the envelope. The results, however, were the same as (3).
5. Seven to ten percent hydrogen in N_2 upper flows of 1 to 15 SCFH and nitrogen lower flow of 8 SCFH -- Nitrogen was used as the lower flow to determine if the formation of the tungsten oxides might have occurred before the burning of the hydrogen in lower hydrogen and nitrogen mixtures. The results were the same as in (3).
6. Seven to ten percent hydrogen in argon 1 to 15 SCFH upper flows and nitrogen 8 SCFH lower flow. Results were the same as (3).
7. Seven to ten percent hydrogen in nitrogen, 2 to 8 SCFH upper flow with a leaktight seal around the exhaust tube and a nitrogen 8 SCFH lower flow. The leaktight seal around the exhaust tube was used to assure that the oxygen entering the bulb envelope was not entering from the top of the exhaust tube. The upper flow rate was restricted to 8 SCFH because higher rates caused the bulb envelope to bulge at the instant of the press seal. The results were the same as (3).
8. Hydrogen upper flow of 1 SCFH and nitrogen lower flow of 8 SCFH -- Pure hydrogen was used in place of the hydrogen-nitrogen mixture to increase the reducing ability of the upper flow. The results were the same as (1). The undesirable turbulence effect of the upper protecting gas with air inside the envelope would be expected to be even greater with the use of pure hydrogen as compared to the use of the more dense 10 percent hydrogen in nitrogen mixture. The increased turbulence

is believed to be counteracted by the greater reducing capability of pure hydrogen to an extent such that acceptable clean tungsten results from the press seal operation.

9. Hydrogen 0.5 to 5 upper flow with a leaktight seal on the exhaust tube and a nitrogen 8 SCFH lower flow. The filament and slip coils had a cover of WO_2. The cause for this oxidation is believed to be an increase in the hydrogen flow through the envelope since none of the H_2 leaked at the connection of the upper chuck and the exhaust tube. The increased flow would cause most of the H_2 to flow through the center of the envelope without spreading out to the walls.

10. Nitrogen, upper flow of 15 SCFH and lower flow of 8 SCFH with a N_2 atmosphere surrounding the bulb envelope during the press operation provided by a 90 SCFH total flow through eight lines of one-quarter inch tubing aimed up from around the base. The N_2 atmosphere was also tested in an attempt to produce a bulb with cleaner tungsten than the minimum standard from the press operation. Still, the results were the same as (1).

11. Hydrogen 1 SCFH upper flow and nitrogen 8 SCFH lower flow, with the N_2 atmosphere surrounding the envelope. This result also was the same as (1).

Conclusion: With a tight connection to the exhaust tube and clean flush gas, the source of oxygen is inhalation of air and combustion gases at entrance of lower end of body glass. The only real solution is elimination of localized variable velocity areas. This can be accomplished by inserting flush needle up into lamp for up flush and retract needle at press position.

18.4 METHODS OF HEATING QUARTZ

There are several methods of heating. Each method will be examined because each has advantages and disadvantages. To cover the range of lamps and quartz sizes it might be necessary to employ more than one method of heating.

MEANS NUMBERS	UPPER PROTECTION	TIGHT EXHAUST TUBE SEAL?	LOWER PROTECTION	TUNGSTEN CLEANLINESS
1	N_2 15 CFH	No	N_2 8 CFH	Good
2	Ar 15 CFH	No	Ar 8 CFH	Good
3	7-10% H_2 in N_2 1-15 CFH	No	7-10% H_2 in N_2 8 CFH	Bad
4	7-10% H_2 in Ar 1-15 CFH	No	7-10% H_2 in N_2 8 CFH	Bad
5	7-10% H_2 in N_2 1-15 CFH	No	N_2 8 CFH	Bad
6	7-10% H_2 in Ar 1-15 CFH	No	N_2 8 CFH	Bad
7	7-10% H_2 in N_2 2-18 CFH	Yes	N_2 8 CFH	Bad
8	H_2 1 CFH	No	N_2 8 CFH	Good
9	H_2 .5-5 CFH	Yes	N_2 8 CFH	Bad
10	N_2 15 CFH	No	N_2 8 CFH + N_2 ATMOS.	Good
11	H_2 1 CFH	No	N_2 8 CFH + N_2 ATMOS	Good

Table 18.3.2 Filament Protection Means Comparison

18.4 Methods of Heating Quartz (Continued)

1. Gas - oxygen burners - direct - premixed.
2. Gas - oxygen burners - direct - surface mix.
3. Gas - oxygen burners indirect and surface mixed.
4. D.C. Plasma torch.
5. D.C. Plasma torch plus electric arc.
6. RF Plasma inside heating.
7. RF Plasma outside heating.

18.4.1 Gas Oxygen Burner - Direct - Premixed

The present method of heating quartz is a circular burner - actually two semi-circulars with multiple holes in multiple tiers. The gas-oxygen is premixed with standard venturi mixers. The burner is made of brass and water cooled.

Disadvantages

1. As with any gas-oxygen burner, the temperature and the flame varies with respect to the burning jet of the flame. The hottest point is about 3/16" in front of the apex of the burning jet or cone. From the hottest point the flame temperature goes down quickly in either direction. There can be temperature differences in the flame of 2000°C. Therefore, the concentricity of the burner and the diameters of the burner with respect to the quartz tube are very important for uniform heating.
2. The thermal conductivity of quartz is very low. Therefore, even with a lot of burner holes, the quartz is overheated at burner holes and remainder is actually heated by burner splash and escaping hot gases.

18.4.2 Gas - Oxygen Burner - Direct - Surface Mix

The original burner design for the Thorn press seal machine was a gas-oxygen surface mix burner. The burners oscillate in an attempt to heat the quartz tube uniformally.

A surface mix burner is one which feeds the gas and O_2 such that they meet in front of burner tip rather than inside burner tip as with premixed gases.

Advantages

1. No venturi mixers required.
2. No blow backs.
3. Cool running burner tips.
4. Large range of adjustment.

Disadvantages

1. Flame not as sharp.
2. Flame harder to aim.

18.4.3 Gas - Oxygen - Indirect - Premix or Surface Mix

An indirect burner is somewhat similar to a rocket nozzle. That is the combustion takes place in a chamber and the hot gases escape through an orifice. In this case, the escaping hot gases become the heat source.

For press seal, a water cooled circular burner with a slot of such dimensions needed to heat area of quartz required would be made with a combustion chamber behind slot.

Advantages

1. The temperature of gases heating quartz would be quite uniform.
2. Present hot spots due to direct flame would be eliminated.
3. Either premixed or surface mixed gases can be used. Probably surface mix would be best for flexibility and elimination of flashbacks and mixers.
4. Good uniform heating of quartz.

Disadvantages

1. Very hot running burner - good water cooling a must.
2. High pressure gas necessary - gas and oxygen probably equal pressure 10 to 20 psi.
3. Probably more noise than present.

18.4.4 D.C. Plasma Torch

The D.C. Plaxma torch heats quartz by heated gases. The gases have been heated by a D.C. electric arc in a chamber inside torch. The D.C. arc has replaced gas and O_2 combustion as a heat source.

To press seal with a D.C. Arc torch, the torch must either supply a slot with hot gases as in the indirect gas-oxygen burner or the torch or torches must oscillate.

Advantages

1. Most any gas or gas mixture may be used.
2. Gas temperature as high as 20,000°F can be achieved. Power and gas type determine temperature.
3. Changes in Beta count of quartz at press sealing can be eliminated.
4. Uniform temperature of heating gases - no hot and cool spots as in flames.
5. Very quick heating of quartz.

Disadvantages

1. D.C. Power supplier required.
2. Difficult to turn on and off for cycling - gas flow at start and run are different.
3. Difficult to apply to circular slot burner.
4. At least two torches required for each set up and the torches would need to oscillate to heat full surface of quartz tube uniformally before pressing.

18.4.5 D.C. Plasma Torch Plus Electric Arc

This method of heating involves a D.C. torch heating with the heated and ionized gas and then adding an arc between the D.C. torch and either a ground electrode or another D.C. torch. The quartz is then heated by the plasma and the direct arc. This results in very high temperatures and heating rates.

Advantages

1. Very high heating rates.
2. Clean heating - no combusion products.

Disadvantages

1. Uniform heating on small diameter tubes only - difficult to control geometry and position of arc.

   NOTE: Philips patent #3,852,053 indicates this type used for tipping 4 mm exhaust tubes on quartz lamps.
2. Two D.C. power supplies required.
3. A lot of U.V. in heat source.

18.4.6 R.F. Plasma - Inside Heating

The R.F. Plasma heats by ionizing gases in a chamber resulting in an induced plasma arc which heats the exit gases.

For press seal purposes, the sheath gases would be eliminated and quartz would be allowed to heat. Of course, any filament or electrodes present would get hot also. Therefore, as in Philips description, the mount would be inserted into quartz after heating and before pressing.

Advantages

1. Quick heating.
2. Uniform heating.
3. Highest heat on inside of quartz tube.
4. Beta count of quartz is usually improved.

Disadvantages

1. R.F. power supply required.
2. Works best on large size tubes (1" dia. or more).
3. Critical positioning of quartz tube to avoid end closing.

18.4.7 R.F. Plasma - Outside Heating

Outside heating is a manipulation of R.F. coil and sheath gases to produce a doughnut shaped arc. The idea would be to design "hole" in arc to fit quartz outside diameter.

Advantages

1. Very high quick heat.
2. Clean heat.

Disadvantages

1. R.F. power supply.
2. Critical placement of quartz tube with respect to doughnut shaped arc.

18.4.8 Plasma and Flame Temperatures

The maximum temperatures normally attained by heat sources are as follows. All sources are suitable for melting quartz in hottest areas of flame.

Combustions

$H_2 + O_2$	.4875°F
$C_3H_4 + O_2$	.5350°F
$CH_4 + O_2$	.4955°F
$C_2H_2 + O_2$	.5625°F
$C_3H_8 + O_2$	.4785°F

Plasma Arc

Air	.16,000°F
Helium	.24,000°F
Hydrogen	6,000°F
Nitrogen	8,000°F
Argon	.19,000°F

Conclusions

1. The same method of heating may not be suitable for large and small diameter lamps and arc tubes.
2. The plasma types will be more valuable where control of Beta is important.
3. The plasma types appear to be best suited for very small diameters and very large diameter quartz tubes.

18.5 CRITERIA OF A GOOD PRESSED SEAL

Several conditions must be met in the press seal of the filament and lead wire set inside the bulb envelope if the bulb is to function properly. The first criteria is that the seal must be hermetic (helium leak rate of less than 1.0×10^{-10} atm cc per second). The other conditions are listed below:

1. The foils cannot be torn; totally or partially. A partial tear would increase the resistance and consequently the temperature of the foil possibly causing the foil to melt at this point, thus creating an open circuit.
2. The quartz glass of the press area cannot have any hairline cracks or chips. These defects could cause a bulb to explode under its high operating pressure and temperature.

3. The moly ribbons must remain parallel. When foils are closer together at the top than at the bottom, the filament legs are slanted toward each other and the filament bows. This condition causes a greater possibility of the filament coils to arc at turn on.
4. The foils cannot buckle. When a foil buckles, it alters the filament position and, therefore, changes the temperature gradient in the bulb. This condition could cause a variety of undesirable results.
5. The bulb must be capable of containing the required pressure of fill gas pressure at room temperature without exploding at operating temperatures. The top of press area inside the bulb, designated as the re-entrance angle has been determined to be the point where all explosions of the bulbs tested originated. Bulbs with the deepest and smallest re-entrance angles are shown to be those which can maintain the least fill pressure. As the angle becomes larger and more shallow, the strength of the bulb increases accordingly.
6. The moly foils and filament must be free of oxides.

It should be noted that the only hermetic seal is the middle area of the moly foil to the quartz. The moly outer leads and tungsten inner leads are not sealed and in fact have a space around them. This space is the result of contraction of the moly and tungsten during cooling. The expansion rate of quartz is 5 compared to about 50 for MO and W. This means that for every degree, the moly wire contracts 10 times as much as the quartz. If the quartz temperature at pressing was 2000°C there would be a space about 1 1/2 mils thick around a 1 mm lead wire at room temperature.

18.5 PRESS FEET DATA

The material is usually #310 Stainless Steel. There is no specific design for press feet. Sometimes the press face is smooth to promote quartz flow and other times it is rough or relieved to minimize flow of the hot plastic quartz under the press faces during pinching or pressing operation.

18.7 GENERAL PRESS SEALING PROCEDURE

A. Attach flush gas line to exhaust tube and insert bulb in holding fixture with open end of bulb down.

B. Insert mount in mount holding jig.

C. Raise mount holding jig to locate mount in desired position.

D. Turn on quartz heating source - usually gas-oxygen or hydrogen-oxygen burners.

E. Continue to heat press area until quartz becomes plastic (1800-2000°C). The temperature can be judged by a device which measures the radiation from the quartz. At working temperatures the quartz is incandescent and must be observed through dark glasses. Since the thermal conductivity of quartz is poor, the quartz must be heated uniformly in press area. This can be done with circular fixed burners, but is usually done with oscillating burners for better coverage.

F. When the quartz has reached the desired plastic state, it must be pressed quickly. Quartz loses heat rapidly at high temperatures due to radiation. The press action must be a press and squeeze to a fixed pressure. That is a mechanical fixed stroke is not desired. The stroke must be spring loaded in case of mechanical press. Air cylinders are most common for quartz pressing.

G. There is no real dwell after final pressure is reached. The press retracts as soon as practical after final pressure is attained.

H. During the heat cycle, the flush pressure was constant and gas flowed out the open end of the lamp. When the glass was pressed, the flow stopped and a flush gas pressure builds up in the lamp. This pressure can cause the bulb to blow out. For this reason, the flush gas pressure is vented just before final lamp closure. After the press (one one or two seconds) the flush pressure is reactivated (not necessarily at same pressure) to form the bulb in seal area -- in fact sometimes the bulb is blown into a mold which is part of the press feet. Even when no forming is desired, the flush gas is activated to maintain an inert atmosphere in lamp during subsequent operations and cooling.

I. After the press, there may be small cracks, scars, etc. on the press and some condensed silica smoke on the bulb. It is common

is common to reheat the press to fire polish the press and to heat the bulb to outgas the quartz, and eliminate silica smoke at the same time.

J. After removal of silica smoke, etc., the bulb can be allowed to cool with the internal flush gas maintained. An alternative procedure is to pump and flush the lamp during cooling. This procedure is suggested because with just the inert flush gas pressure there is no flow. If material outgased into lamp during post heating, it would not be removed and may be reabsorbed by the lamp only to come out later in lamp operation. The inert gas only protects the lamp from contaminants outside the lamp. The flush-pump cooling may be more important for discharge lamps than halogen lamps.

18.7.1 Press Feet Lubrication

The press feet should be lubricated occasionally with Molykote G, MoS_2 suspension. Without any lubrication, hair line cracks can occur especially with the I press.

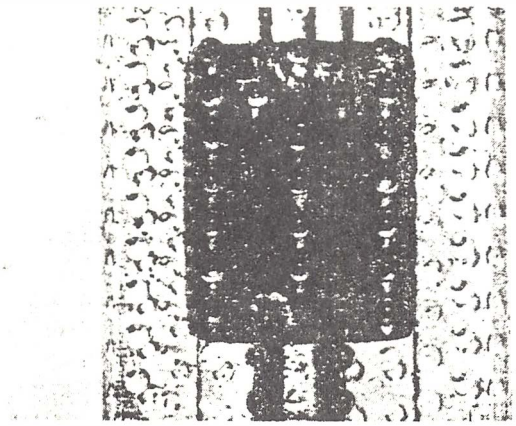
Hairline Cracks

As a result of the lubrication, the press feet need to be cleaned daily with a steel brush.

18.8 PRESS SEAL EQUIPMENT

18.8.1 Single Head - Burner Press

The early (1950) single head machine was a device which held the quartz, a mount holder, the lamp was double end with exhaust tube in the middle and flush gas line was a rubber hose pushed over the end of the exhaust tube. The press area was heated by hydrogen-oxygen burners and when quartz was soft, the burners were used as press jaws. This left the design of the burners on the press (see Figure 18.8.1).



Figures 18.8.4

18.8.2 Single Head - Separate Burner & Press Feet

The burner can be hydrogen-oxygen or gas oxygen. The burner can be circular "V" shaped, "L" shaped, oscillate or even rotate around the quartz during heating. Generally, the burners are water cooled. The bulb is held in a fixed "V" jaw. The mount holder is on a slide such that the mount can be raised up into the bulb. The burners have pilots so that the burners can be solonid controlled. The quartz is heated and the radiation measured by a photocell. The press is activated by the photocell. The press is air cylinder operated. When the press is activated, the burners and flush gas are deactivated.

The rough surface of the older burner press is sometimes machined into one press foot and the other left smooth. This condition is thought to minimize quartz flow during pressing.

18.8.3 Rotary Press Seal

There are as many designs for rotary press seals as there are for single head press seals. The following are general rotary exhaust cycles for single end Halogen lamps and double end mercury arc lamps.

18.8.3.1 Halogen Lamp - Quartz or Vycor

Pre-tubulated bulbs with exhaust tube up are delivered to press seal from the Tubulating Machine.

The Press Seal Machine has two preheat positions with four burners per station. The burners are water cooled with two individual burners in two water cooled burner blocks. The head hangs down from the indexing turret so that the mount block and tubulated bulb can pass between the burners. The two preheat positions are followed by an optional pre-press. The press is air operated. The mechanism is a vertical toggle which makes the jaws radial to the turret. This is followed by two more heating positions followed by the final press. After pressing, there is one annealing position. The upper part of the machine, which contains the exhaust tube and flush tubes, is protected by a heat and silica smoke shield. The exhaust tube is held in a simple lathe type collet and not sealed. Since the flush gas leaked through the collet, there was no blowout on pressing and no vent required. The upper part and collet was water cooled. All fires are individually controlled with flow meters. There are fires in the press positions. On some machines, the fire positions after the pre-press are controlled front and back only. The others, all four burners, are controlled individually. The complete lamp is removed from the press seal leaving the mount block behind. After press seal, some types are flushed with forming gas and filaments are heated electrically to about 1200°C.

18.8.3.2 Rotary Press Seal for Mercury Arc Tubes

1. The rotary press seal requires 3 or 4 operators depending on the type.
   A. Load tubulated quartz and double hairpin.
   B. Unload and adjust probe (optional)
   C. Load single hairpin and rotate arc tube.
   D. Unload, inspect, and cut moly lead wires.
2. Features of the press seal are as follows.
   A. Quartz is loaded into a "V" quartz holder with exhaust tube horizontal.
   B. Seal to exhaust tube is accomplished by use of a "Spool" type compression rubber with high pressure air applied after positive position is established.

C. Three preheat positions plus heat at press station for press positions. Burners consist of 4 burners, pre-mixed gas and oxygen. Each burner consists of 2 vertical rows of 3 holes. Bottom row of holes is positioned 3/16" - 1/4" above bottom edge of quartz. Burners and heads are adjustable for different size arc tubes. The flushing gas is nitrogen. For some lamps, 2-3% H_2 is added to the nitrogen.

D. Rotary plate valve supplies high pressure air, flushing gas and water.

E. The press stations are air operated and relief in press station is provided by dumping, by releasing high pressure air applied to exhaust tube "Spool" compression rubber.

F. In the positions, before unload, the arc tube is vacuum pumped and then filled with argon.

G. Index speed 650/hour.

18.8.3.3 General

GTE Sylvania Equipment Development is developing a new rotary press seal that does not require watercooling. The burners are surface mix (4 in each heating position) and oscillate for uniform heating. The machine has a rotary valve plate like an exhaust machine to allow flexibility of flush pressures at any position. After pressing, pumping and flushing is provided during lamp cooling. The index speed is 1800/hour.

18.9 SILICA SMOKE

Silica smoke is condensed silicon oxide vapor which was evaporated from the quartz. The working temperature of quartz lies between 1800° and 2000 °C. At these temperatures, evaporation of SiO_2 is rapid. The vapor pressure is 10 times as high at 2000°C as at 1800°C.

$$SiO_2 \longrightarrow SiO + 1/2O_2$$

Quartz Temperature - °C	Vapor Pressure - Torr
1000°C	10^{-5}
1220°	10^{-2}
1800°	10
1900°	40
2000°	100
2100°	375

18.9.1 Control and Elimination of Silica Smoke

The data show that the higher the temperature of the quartz, the more silica smoke is generated. For a single operation, the worst condition would be quartz cutting with a CO_2 loser. The very nature of the cutting process is to evaporate quartz from a very narrow band right through the quartz tubing. Tubing cut in this manner does show a rather heavy band of silica smoke buildup on both sides of the cut. The laser cut is high temperature rapid heating.

18.9.2 Slow Heating and Minimum Quartz Working Temperatures

Generally, the quartz surface to be sealed or worked is not the surface being heated. For example, in press sealing it is the inner surface of the quartz tubing that is to be sealed, but in most cases the heat is applied to the outside of the tubing. Since quartz is a poor thermal conductor, the inner surface will take time to get hot somewhat independent of the intensity of the heat applied to the outside. Therefore, for minimum silica smoke, the burner applied to the outside should be at as low a temperature as practical to get the inner surface up to the required temperature for sealing. Sealing time will be longer but silica smoke problems will be minimized.

When the silica smoke is in a vapor state, it can be removed by suction system or it can be blown away from the quartz surface by a gas stream and then trapped by a vacuum cleaner or air extraction system. When silica smoke condenses on a cool plate it becomes a flacky white dust.

18.9.3 Prevention of Adhered Silica Smoke on Lamp

The silica smoke that is a problem is smoke which condenses and sticks to or becomes part of the quartz. The conditions for condensation are a lower temperature, but if the surface temperature is low enough the silica smoke does not adhere.

One method of controlling silica smoke at press seal is to install another set of burners above the press seal burners. The top burners are far less intense than the press seal burners. The extra burners heat the quartz above the press seal to minimize condensation and at the same time blow the smoke away from the quartz with the combustion gases. There has also been success by simply blowing air through the extra burners. Apparently, the movement of the gases in that area is a bigger factor than raising the quartz temperature.

It should be noted that the SiO_2 vapors should be removed from the area of operators in any case. There can be a health problem (silicosis hazard).

18.9.4 Minimizing Silica Smoke by Oxygen Ratio of H_2 - O_2 Burners

It has been found that the generation of silica smoke is much greater when the ratio of hydrogen to oxygen is 2 to 1 than when the H_2 - O_2 ratio is 1 to 2. The reason for this is not clear. The flame temperature is probably lower with the excess oxygen, but there may also be chemical reasons that are not obvious. For example, since silica smoke is mostly SiO and quartz is SiO_2, the oxygen rich flame may tend to keep SiO_2 from converting to SiO.

18.9.5 Removal of Silica Smoke from Lamps

The adhered silica smoke is as much a part of the quartz as an abrased surface or small scratches. There are two common methods of "removing" silica smoke to improve the surface and light transmission of the quartz.

18.9.5.1 Mechanical Buffing

For this method, a motor driven buffing wheel and fine abrasives (jewelers rouge) are used. This work is done by hand at final inspection of lamps.

18.9.5.2 Fire Polish

The surface of the quartz must be heated to the point where the smoke will melt and fuse to the quartz as a smooth clear surface. The temperature must be kept as low as possible in order to keep from generating more smoke. Usually the lamp is heated beginning just above press and effectively chases the smoke up and off the end of the bulb. It is possible to heat the quartz enough to clean up silica smoke inside the lamp, but it is a slow process and not usually recommended.

18.9.5.3 Chemical Treatment

The surface of quartz can be etched by hydrofluoric acid (HF) and also by Phosphoric acid. (See section 15.2.1.2 Quartz Cutting).

18.10 References for Additional In-Depth Information

1. Materials of High Vacuum Technology by Werner Espe, Vol. II, The Silicates, Pergamon Press.
2. Method of Making Discharge Lamp Having Blow-Molded Arc Tube Ends - General Electric. U.S. Patent #3,939,538 (1976)
3. Quartz Lamp Sealing Machine - General Electric U.S. Patent #2,857,712 (1958)
4. Quartz Tube Pinch Seal - General Electric. U.S. Patent #2,965,689 (1960)
5. Quartz Lamp Sealing Machine Control - General Electric U.S. Patent #3,079,775 (1963)
6. Method of Sealing Quartz - U.S. Philips U.S. Patent #3,852,053 (1978)
7. Heating Quartz Glass with a Plasma Torch and Press Sealing Philips Tech Review 34, No. 2 (1973)

19.0 PUMPING AND FILLING HALOGEN LAMPS

The general process is no different than any other incandescent lamp and can be done on a trolley exhaust or on a rotary exhaust machine at speeds of 2000 indexes per hour or more.

The process varies depending on lamp type and fill gas. In some cases, the entire cycle may be 3 or 4 flushes with dry nitrogen, then pump to about 1 Torr, fill and tip. In other cases, the cycle is quite elaborate. Sometimes, the lamp is trollied or cleaned up on one machine and then transferred to the final vacuum and filling equipment.

The following is a complete exhaust cycle. All of these steps are not necessarily recommended for all lamps, but some critical lamps may require the complete cycle.

Load

Pump

Leak Check

Pump to approximately 1 Torr

Flush to 800 Torr with N_2

Pump to approximately 10 Torr

Flush to 800 Torr with N_2

Pump to approximately 10 Torr

Flush to 800 Torr and light filament to dull red for initial outgas of filament.

Heat with gas-air burners - 3 or 4 positions

Pump to 10 Torr

Flush to 800 Torr with N_2 + 1% CH_4 (Methane) and light filament to 1000 - 2000°C.

Pump to 10 Torr.

Flush with Forming Gas and light at about 95% of rated volts.

Pump to less than 1 Torr

Fill with halogen dosed gas

Cool with liquid N_2

Tip

19.1 EQUIPMENT CONSTRUCTION MATERIALS

For best results with all halogens, stainless steel or monel should be used for metal parts and Viton (fluorocarbon rubber) should be used for seals etc. Pump oils and valve plate oils are affected differently by the different halogens. For HBr, pump oil must be changed quite frequently. Valve plate oils can be flushed out as often as necessary - (about 4-6 weeks with HBr.)

19.2 EQUIPMENT DESIGN FEATURES

The exhaust head usually has 2 valves. One valve is the normal sweep valve. The other is the fill valve. The fill gas does not usually go through the valve plate -- there is bromine lamp equipment that is exactly like the regular incandescent lamp exhaust and makes good lamps. In Europe, it is common to mount the dosed fill gas tank on the turret.

In the United States it is common to have a rotary "O" ring valve in addition to the plate valve. The "O" ring valve supplies a fill manifold which in turn supplies each head. The advantage of the "O" ring valve is that bigger fill gas tanks can be used and ease of switchover from one tank to another.

The cooling is always liquid nitrogen. However, it may be a bath for complete lamp immersion -- this method is universal or it may be a bubble or spray to cool a single spot on the lamp. The spray method is most applicable for Krypton or Xenon.

Nitrogen cannot be condensed by liquid nitrogen. For this reason, maximun fill pressure at room temperature is approximately 3 atmospheres.

19.2.1 Liquid Nitrogen Cooling - Immersion vs Spray

When a lamp is first immersed in a liquid nitrogen bath, a vapor barrier is formed near the bulb due to rapid evaporation of the liquid nitrogen as it approaches the warmer bulb. This results in an approximate 10 second delay before any pressure drop in lamp

is noticeable due to cooling of the fill gas. In the case of the liquid nitrogen spray, a small jet of liquid nitrogen under pressure is directed at a small spot near base of lamp. The force of the jet breaks through the vapor barrier and contacts the bulb directly. The net result is that the lamp pressure starts to drop in approximately 4 seconds. However, once the whole lamp is cold due to immersion, the pressure starts dropping faster because of a much-much larger cold surface and starts catching up to the spray process and soon passes it in the case of oxygen and argon filled lamps.

The following tables show the lamp pressure vs time for Krypton, Oxygen and Argon filled lamps for immersion and spray cooling processes.

KRYPTON

Time (Sec.)	Pressure(Torr Immersion)	Pressure (Torr Spray)
2.5	800	800
5.0	800	400
7.5	800	125
10.0	700	10
15.0	125	10
17.5	10	10
OXYGEN		
5	800	800
7.5	800	675
10	675	600
15	275	460
20	210	300
25	170	225
30	170	200
33	170	170

ARGON

Time (seconds)	Pressure(Torr) Immersion	Pressure(Torr) Spray
5.	800	800
7.5	800	700
10.0	800	625
15	450	500
20	250	375
25	250	300
30	250	250

The data show that the spray process is superior for Krypton only. The spray nozzel design and liquid nitrogen transport system require specially designed equipment. For details contact Equipment Development, GTE Sylvania, Ipswich, Massachusetts, or Vacuum Barrier Corp., Four Barten Lane, Woburn, Massachusetts 01801

19.3 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

1. Method of Manufacturing Gas Filled Lamps, N.V. Philips, U.S. Patent #3,788,724 (1974).

2. Method of Sealing a Quartz Tube, N.V. Philips, U.S. Patent #3,852,053 (1974).

3. Exhaust and Filling Machine for Lamps, G.E., U.S. Patent #2,870,596 (1959).

20.0 OUTER MOUNT WELD OXIDIZATION PROTECTION

The life limiting feature of long life halogen lamps is often the failure of the weld of the outer moly lead to the moly sealing foil. In general, the higher the seal temperature - the shorter the life of the lamp or seal life decreases as seal temperature increases.

Most hermetic seals are satisfactory to a seal temperature of approximately 350°C. Beyond the temperature of 350°C an oxidation reaction between the oxygen in the surrounding atmosphere and the molybdenum foil or other oxidizable foliated material usually takes place and damages the lamp by substantially reducing its usable life. The oxidation reaction takes place because microscopic passageways formed around the lead wires permit oxygen to enter the foil area of the lamp. These passageways are formed because of several characteristics of hermetically sealed lead-in conductors.

In the pinch seal operation, the quartz does not totally attach itself to the relatively heavier outer and inner lead wires. The reason for the microscopic passageways, which exist not only along the outer lead wire but also along the outer edge of the foliated portion, is the substantial difference in the coefficient of thermal expansion of the quartz compared to that of the outer lead wire which is usually tungsten or molybdenum.

There are several methods of making the outer mount weld more resistant to oxidization.

20.1 PLATINUM PLATED OUTER LEADS

The high cost of platinum and the difference in its coefficient of linear expansion as compared to moly (the coefficient for platinum is approximately twice that of moly) are drawbacks. In addition, platinum has poor heat conduction and higher electrical resistivity than moly. The melting point of platinum is 1773°C or below the working temperature of quartz. This results in melting and flow of the platinum when the press seal is made.

Platinum plated outer lead parts is an improvement over no protection at all.

20.2 MOLY PHOSPHIDE COATINGS

Coatings of molybdenum or tungsten phosphate glasses, as well as molybdenum or tungsten phosphides adhere firmly to surfaces of refractory metals such as molybdenum and tungsten, e.g., in wire, foil or other form, and protect them from oxidation in air up to temperatures of approximately 800°C over long periods of time and up to approximately 1200°C for periods of minutes. In addition, such coatings dissolve the oxides of molybdenum and tungsten, thus serving as a flux to create clean, wettable metal surfaces for bonding, and at the same time, they are completely wettable by the silica and silicates of which the lamp envelopes are formed, thereby facilitating the formation of sound press seals.

There are several ways to prepare the phosphide coating. The most direct is to put a small amount of dry red phosphorous and the parts to be coated in a quartz vessel, evacuate the vessel to 1 Torr or less, tip off and heat the assembly in an oven at about 800°C for one to several hours depending on the desired thickness of moly phosphide coating. Caution: When breaking open the quartz vessel to remove the coated parts, immerse the quartz vessel in a water bath. The vessel will contain some white phosphorous which will ignite on exposure to air.

The major problem with the phosphide coating is that the melting point is less than moly and too close to the working temperature of the quartz (1800 - 2000°C). The result is very critical press sealing with more than normal split moly ribbons.

An alternative which has been tried with some success is to coat the moly parts after the press seal and lamp is complete. To coat the outer lead exposed areas, the entire lamp has to be put in the quartz vessel and treated like the moly foils above. This operation is awkward and expensive, but it does work and may be suitable for small lamps used in extreme high temperature applications.

20.3 CHROMIUM COATINGS

The chromium coating cannot be sealed to the quartz. Therefore, only the oxidizable half of the moly foil is coated with a chromium film.

The chromium coating is deposited on only one-half of the moly foil and lead assembly by a diffusion process wherein the area to be coated is submerged in a boat which contains chromium and alumina.(See Fig. 20.3.1)

Alumina is used to disperse the chromium particles and does not enter into the chemical reaction which produces the oxidation-resistant film. The assembled conductor is submerged in the powdered chromium and alumina until approximately one-half, or some other desirable portion, of the foil remains above the powdered surface. The boat or container is then placed into a furnace the temperature of which is at approximately 1000°C. A gaseous mixture of hydrogen and hydrogen chloride gas is flowed through the furnace for approximately 5 minutes. During the gas flow, chromium reacts with the chlorine in the gas to form chromous or chormic chloride which then decomposes when it comes into contact with the molybdenum. The chromium from the decomposed chromous or chromic chloride combines with the molybdenum to form the oxidation-resistant film.

Seal life increases at 450°C from 600 hours to 5000 hours; at 500° from 200 hours to 2000 hours; at 550°C from 100 hours to 825 hours and at 600°C from about 50 hours to 600 hours.

This coating procedure is used in production on special lamps both in the United States (GE) and in Europe (Osram).

20.4 SANDBLASTING WITH ALUMINUM OXIDE

It has been found that sandblasting the outer parts of foil and lead assembly with aluminum oxide increases the oxidization resistance of the moly foil and weld. The mechanism is not fully understood, but may result in a coating of AlO_3 due to the high velocity particles impending on the surface of the moly. It is also possible that the moly surface has been "filled" and may be more dense by the aluminum oxide shot peening.

20.5 OXIDIZATION PROTECTION BY CLOSING VOIDS WHICH ALLOW OXYGEN TO PENETRATE SEAL AREA

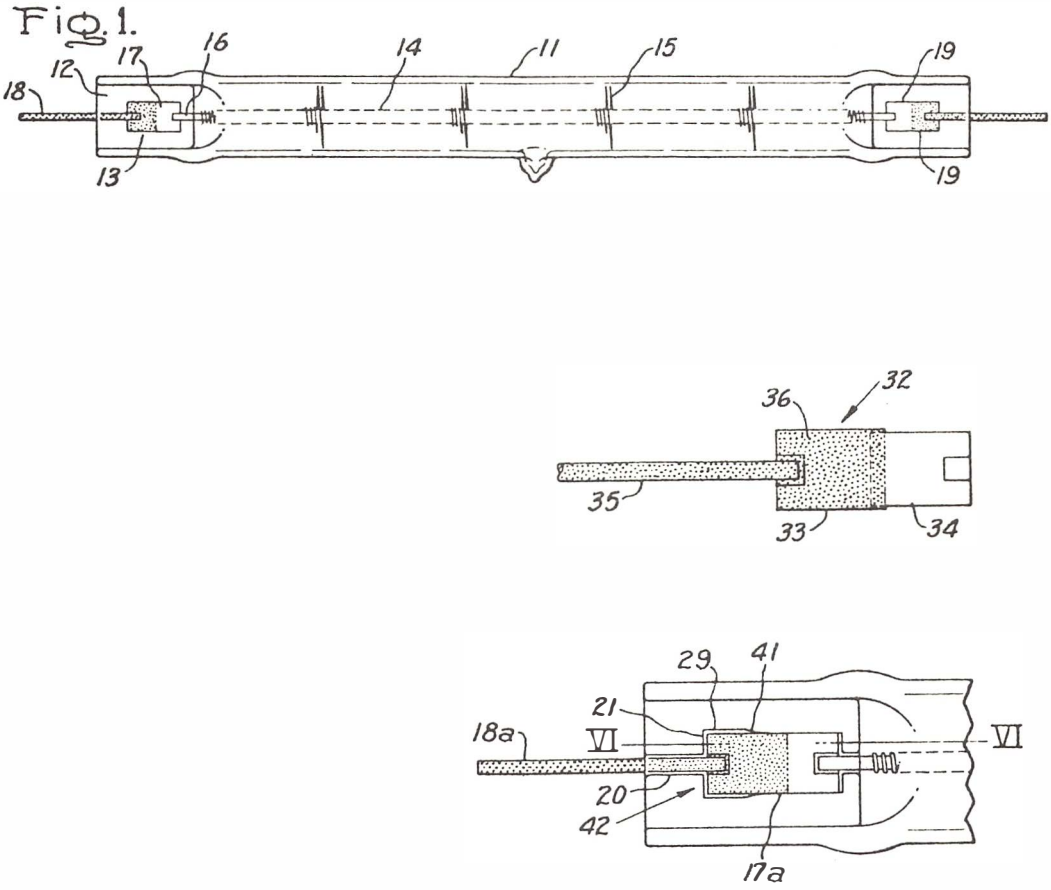


Figure 20.3.1
Chromium Coating

20.5.1 Glass Plugs

The oxidization protection is achieved by providing an effective oxygen barrier in the form of a glass bead on each of the outer lead wires. The bead is completely embedded in the quartz pinch and is composed of glass having relatively low expansion which may be about the same as, or not substantially greater than about four times that of the quartz and which has a softening temperature significantly less than that of the quartz but above 700°C.

In some cases, the beads are attached to the leads before press sealing. In other cases, the beads are added after press seal is complete. Thorn LTD adds the beads to the finished lamp.

The glass beads are of a composition such that they seal to the fused silica or quartz pinch seal by virtue of a close expansion match. They soften at a temperature enough lower than quartz that they deform during the pinch sealing and fill what would otherwise be open channels between the lead wires and the quartz, thus effecting a barrier against the penetration of air into the seal, and they form a sufficiently strong bond to the lead wires such that in spite of an expansion mismatch with the wire, an effective oxygen barrier is maintained.

Accordingly, the glass of the beads should have a coefficient of expansion which may be about the same as that of fused silica or quartz or not substantially more than about four times greater, that is not greater than about $23 \times 10^{-7}/°C$ and prefereably less than 15×10^{-7}.

The softening point may be within a relatively wide range as long as the thermal expansion requirements are satisfied; the upper limit may be about 1300°C in order to insure that the viscosity is sufficiently low at sealing temperatures to allow good flow characteristics; and the lower limit should be above about 700°C, in order that the viscosity of the glass during sealing is high enough to prevent it from completely running out of the seal area.

Referring more particularly to the composition of the glass beads, by way of example, the above requirements are found in a family of copper-alumino-silicate glasses having a composition, in percent by weight, within the approximate range given in the following table:

TABLE 1

	Percent
SiO_2	33 - 66
Al_2O_3	11 - 28
Cu_2O	20 - 39

Another family of glasses useful for the beads are some of the various well-known graded seal glasses which are generally borosilicate or alumino-borosilicate glasses containing little or no alkali and which may have compositions within the range, by weight, given in the following table:

TABLE 2

	Percent
SiO_2	75 - 85
Al_2O_3	1 - 10
B_2O_3	8 - 13
Na_2O	0 - 0.8
K_2O	0 - 0.5
BaO	0 - 3.5
CaO	0 - 3.5

By way of example, tests were conducted on a halogen cycle lamp of the single-ended type of 1000 watt rating and having a design life of 500 hours. The beads were of copper-alumino-silicate glass and the lamp was operated with the seal at a temperature of about 450 - 500°C. The lamp failed due to normal filament burn-out at 411 hours with no hint of foil oxidation. Without the glass beads and based on knowledge accumulated from previous test results, the lamp would have been expected to fail due to seal oxidation at a life ranging from 40 hours to 200 hours.

20.5.2 Metal Plugs - N.V. Philips Patent (German)

The oxidization protection is achieved by providing an effective oxygen barrier in the form of a metal plug on each of the outer lead wires. The metal plugs have a melting point between 600 and 1500°C.

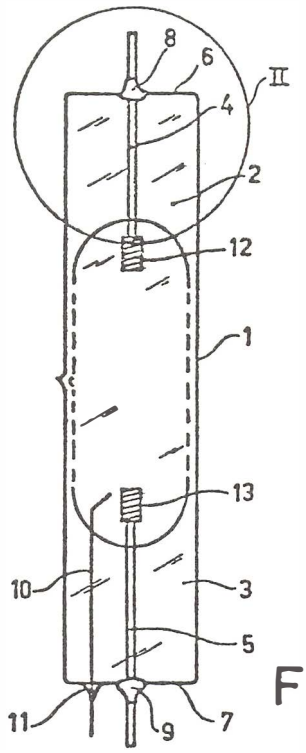


FIG.1

Around the external conductor there is a capillary space which extends to the moly ribbon, through which oxygen and moisture can reach the leaf. In this way the leaf can oxidize and the stem-press can crack.

The metal plug contains at least one metal from the zinc and lead group mixed with at least one metal from the group consisting of titanium, zirconium, hafnium, niobium, tantallium, and vanadium, the weight ratio between the first and second metals being 100:0.05 to 100:1, and the metal plug is welded to the glass of the stem-press.

The melting point of the metal of the plug is approximately 235°C for plugs containing only zinc as the first metal, and increases in proportion to the quantity of lead in plugs containing only lead as the first metal.

20.6 LONG PRESS SEALS

Since it is the press seal temperature that determines the seal life due to oxidation, a reduction in temperature at the outer lead weld will have a major impact on seal life. The press seal temperature is a result of heat dissipated from the filament and I^2R loss in the moly ribbon itself. Assuming the ribbon is of proper size for its running current, one way of reducing the temperature is to get the seal further away from the heat source (the filament). This can be done by using longer moly ribbons and a longer press seal. In one example, the moly ribbon was increased from 7 mm to 13 mm in length and the temperature dropped from 550°C to 430°C and average seal life increased from 30 hours to 66 hours.

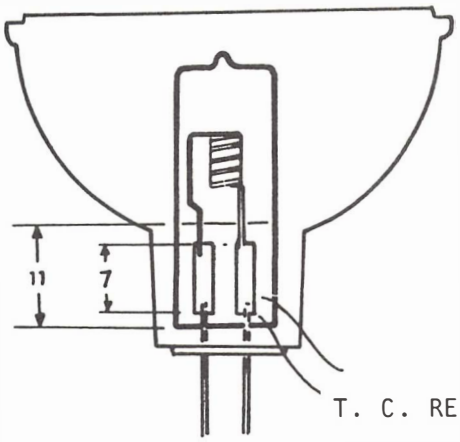
MANUFACTURED TYPES WHERE LONG SEAL TECHNOLOGY HAS BEEN USED:

TYPE	WATTAGE	PREVIOUS LIFE	LIFE NOW	RATED
ECL	250	35	50	50
FAD/FBX	650	50	100+	100
FAL	420	50	75+	75
ENX	360	60	75	75

RN 153

CODE 4646

OPERATING IN CAROUSEL



T. C. READS 550°

SHORT FOIL

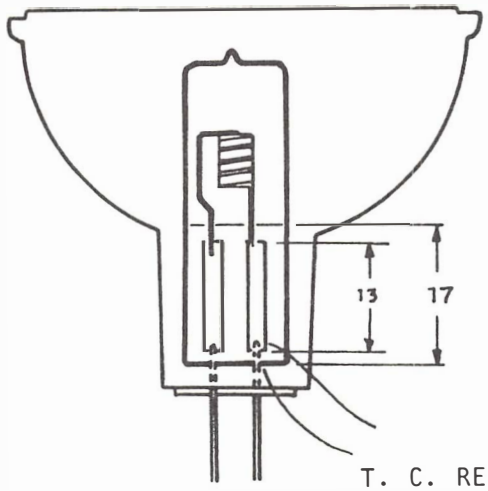
LIFE	FAILURE MODE
47.4	PRESS SEAL
46.7	PRESS SEAL
33.2	PRESS SEAL
18.1	PRESS SEAL

$\overline{X} = 36.3$

LONG FOIL [NO PRESS FAILURES]

LIFE	FAILURE MODE
77.5	NORMAL
72.4	NORMAL
66.4	NORMAL
58.5	NORMAL
55.0	NORMAL

$\overline{X} = 65.9$



T. C. READS 430°C

20.7 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

1. Electric Incandescent Lamps Having Refractory Metal Phosphate and Phosphide Coatings for Refractory Metal Leads GTE U.S. Patent #3,723,792 (1973)

2. Process for Producing Lamps with Oxidization Resistant Leads GTE U.S. Patent #3,785,019 (1974)

3. Quartz to Metal Seal for Electrical Devices GE U.S. Patent #3,515,420 (1968)

4. Lead in Conductor for Electrical Devices GE U.S. Patent #3,420,944 (1966)

5. Oxidization - Resistant Lead-in Conductors for Electrical Devices GE U.S. Patent #3,793,615 (1974)

6. Electric Lamps, N.V. Philips German Patent #29-38-163 (March 1980)

21.0 HALOGEN LAMP FUSES

There are many considerations for the design of a fuse for halogen lamps or any other incandescent lamp.

The first requirement for a fuse is to withstand the inrush current at turn on for a short time. The general rule is that the maximum inrush current is 11 - 12 times the operating current.

The second requirement for a fuse is that it will fail (clean or blow) when arcing occurs due to filament failure.

An additional requirement is that the fuse will not change its initial characteristics during the life of the lamp.

21.1 FUSE LOCATION

Some fuses are in the lamp itself. Trufocus projection lamps have an internal fuse. In this case, the fuse is covered with a glass tube to keep molten metal from impacting the lamp body and possibly cause a stress leading to bulb failure and explosion.

GLS lamps have the fuse in the lamp base. The fuse is usually the lead to the center contact. Some lamps, especially European lamps are double fused.

Long linear double ended halogen lamps are not fused at all. Low voltage (automotive) lamps and vacuum lamps do not require fuses.

External fuses are the most popular and are the most problem because the vaporizing of the fuse can cause an arc in the lamp base which can destroy the lamp base and socket.

21.2 FUSE MATERIALS

The fuse material is chosen for:

a. Current capacity vs size
b. Oxidization or corrosion resistance
c. Cost
d. Welding ability to dumet
e. Soldering or welding ability to base and center contact.

Some of the fuse materials are as follows:

NiD

Ni

Monel

Alloy 52

Copper NiPlated

Everdur

Everdur NiPlated

Dumet (Unborated)

Dumet (Borated)

21.3 FUSE DESIGN

The parameter that is most useful in studying fuse characteristics is I^2t where I is the RMS current and t is the burn out time. First, it is an indication of the energy required to melt a fuse. Second, it is a constant for a wide range of high current values. Actually, the I^2t for the clearing of a fuse can be divided into two parts, namely melting and arcing. The arcing I^2t contribution is usually negligible until sub cycle melting occurs.

If the radiant heat and end effect heat losses are ignored, then the heat necessary, Q_m, to melt a fuse is given as follows:

$$Q_m = mc\ (T_m - T_o) + mL, \quad T_m > T_o$$

where m is the mass of the fuse,

c is the specific heat,

T_m is the melting point temperature,

T_o is the ambient temperature, and

L is the latent heat of fusion.

The source of energy for Q_m is heating. Thus

$$I^2Rt = mc\ (T_m - T_o) + mL$$

where I is the rms current,

R is the average resistance, and

t is the time elapsed for melting.

Furthermore, for a fuse of uniform cross-sectional area, A, and length, l, the resistance is given as follows:

$$R = \rho \frac{l}{A}$$

where ρ is the resistivity of the substance.

For metals in the temperature range such that,

$$T_o >> \theta$$

where θ is the Debye temperature of the metal then

$$\rho = KT_o$$

where K is a constant related to atomic parameters.

The Debye temperature is a characteristic of a material and it makes the point in temperature where the resistivity of a metal radically changes.

The following table lists some representative values of the Debye temperature:

TABLE I

Representative Values of θ *

Compiled P. Keesoom and N. Pearlman

Substance	^oK	Substance	^oK	Substance	^oK
Be	1160	Fe	467	Al	418
Mg	406	Cu	445	In	109
Ca	219	Ni	456	Tl	89
La	132	Pb	275	C(Diamond)	(2000)
Ti	278	Pt	229	Si	658
Zr	270	Cu	339	Ge	366
V	273	Ag	225	Sn(Gray)	212
Nb	252	An	165	Sn(White)	189
Ta	231	Zn	308	Pb	94.5
Cr	402	Cd	300	Bi	117
Mo	425	Hg	(60-90)		
W	379				

Note that for a given material at a constant T_o, I^2t is independent of the fuse length (l), when l is greater than 2.5mm, and is directly proportional to the area squared, A^2. Now if A is fixed, then I^2t is inversely proportional to T_o (ambiant temperature).

It is reasonable to expect that a given lamp type will explode when the arcing power is above a certain value, and conversely the lamp will internally quench the arc when the power is below that value.

Actually there are two limits for the selection of a fuse. The lower limit is set by the I^2t value associated with the inrush current. The upper limit is the I^2t value at which the lamp explodes. The inrush I^2t was empirically found to be given as follows:

$$I^2t \simeq 60I_o^2 \quad \text{in } (\text{amp}^2 \text{ X \# of cycles}),$$

where I_o is the normal operating current through the lamp. This rule of thumb was found to hold over the range of lamps tested, namely 250W to 1500W.

I^2t can be expressed in Amp^2 seconds or in Amp^2 X # of cycles as in 60 cycles/second.

At the present time, it appears impossible to predict an operating pressure and percentage of fill gas which can make a wide range of lamp types stable during arcing.

If, however, the power during arcing is minimized, then the inrush limitation is adequate to select a fuse for a given lamp.

LAMP WATTAGE vs FUSE SIZE

Lamp Wattage (120V)	Fuse Size
15W CA9	.009
25W CA9	.009
40W CA9F15	.009
50W R20	.009
60	.009
75	.010
100	.010
150	.012
200	.012
250	.014

It is important to consider actual I^2t values for existing fuses and the dependence of I^2t on the fuse geometry and ambient temperature.

I^2t should be directly proportional to the square of the fuse cross-sectional area when ambient temperature T_o is constant.

Thus for a fuse wire, it is expected that
I^2t = (constant) d^4 where d is the diameter of the fuse wire.

The following table is measured I^2t for different diameters of fuse materials in air at room temperature.

Material	Diameter (mils)	I^2t	d^4 X (constant)	
Monel - 400	10	40	40	K = .004
	12	76	82.9	
	14	140	153.6	
	16	230	262.1	
Ni D	10	61	61	K = .0061
	12	120	126.5	
	14	210	234.3	
NiPlated Fe	12	137.5	137.5	K = .00663
	14	260	254.7	
NiPlated Dumet	10	75	75	K = .0075
	12	150	155	
	14	270	288	

The data show that each material has a specific constant and that I^2t does vary as d^4 and that I^2t increases with (K) for a given fuse dia.

Material	K
Monel-400	0.004
Ni D	0.0061
Ni Plated Fe	0.00663
Ni Plated Dumet	0.0075

Since each material has a specific constant, it is possible to calculate the dia. of various fuse materials for equal I^2t characteristics.

Material	Diameter (mils)	Burnout Current
Monel	10	5.3 A
NiD	9	5.3A
Nickel Plated Fe	8.8	
Nickel Plated Dumet	8.5	

I^2t Variation with Ambient Temperature

12 Mil Diameter Nickel Fuse with 60 cycle per sec. Power Supply

Temperature	I^2t
183°C	9000
225	8000
250	7600
300	6900
350	6500
400	6100
500	5500
1000	4500

The data show that I^2t varies inversely with temperature.

$$I^2t \text{ varies as } \frac{1}{\text{Temp.}^{.4}}$$

Since the lamp current is constant, the variation in I^2t is due to time or the higher the ambient temperature the shorter the blow time.

FUSE TEMPERATURE AS A FUNCTION OF CURRENT

The fuse leads are 12 mils in Ambiant Air

Fuse Material	Current	Fuse Temperature
Monel 400	1 Amp	100°C
NiD	1	48°C
NiPlated Fe	1	39°C
NiPlated Dumet	1	34°C
Monel 400	2 Amp	250°C
NiD	2	150°C
NiPlated Fe	2	95°C
NiPlated Dumet	2	67°C
Monel 400	3 Amp	440°C
NiD	3	310°C
NiPlated Fe	3	290°C
NiPlated Dumet	3	135°C

The data show that the variation of fuse temperature due to current varies with the material.

21.4 ARCING POWER vs LAMP FILL GAS PRESSURE

The following table shows power during arcing (P) vs the Operating Pressure for 20% and 30% Nitrogen Fill in a 500 watt lamp.

Pressure	P (20%N_2)	P (30%N_2)
6.5 Atmos	13.5 KW	10 KW
13.0	8.5	6.3
26	5.45	4.0

The data show that the power at arcing varies with pressure and composition of fill gas. For this example:

$20N_2$ 80A varies as $\dfrac{1}{\text{fill pressure}^{.65}}$

$30N_2$ 70A varies as $\dfrac{1}{\text{fill pressure}^{.66}}$

The arcing power vs % Nitrogen in fill gas in this example decreases as % N_2 increases in a linear manner. More data are needed for a complete picture.

21.5 CRIMPED OR ROLLED FUSES

Since the length of a fuse longer than 2.5mm does not change the characteristic of the fuse, it is reasonable that a short reduced section in a lead wire will be the failure point and further, that the arc will not be maintained once the short section has been evaporated.

a. Fuse Crimp - This fuse is formed by compressing the lead wire between two hydraulically actuated carbide rods (1/8" diameter). This method is preferred for lamp making due to its high speed adaptability to automount manufacturing rates. However, the fuse when formed can only withstand limited flexing due to subsequent fracture. This is acceptable for lamps that do not involve manual assembly operations.

b. Fuse Flat - This fuse is formed by compressing the lead wire between two hardened rolls which then roll along the wire for a certain distance, compressing the wire as they roll. This method is slower and less adaptable to the automount but the resulting flexural strength of the fuse section is greater than the fuse crimp.

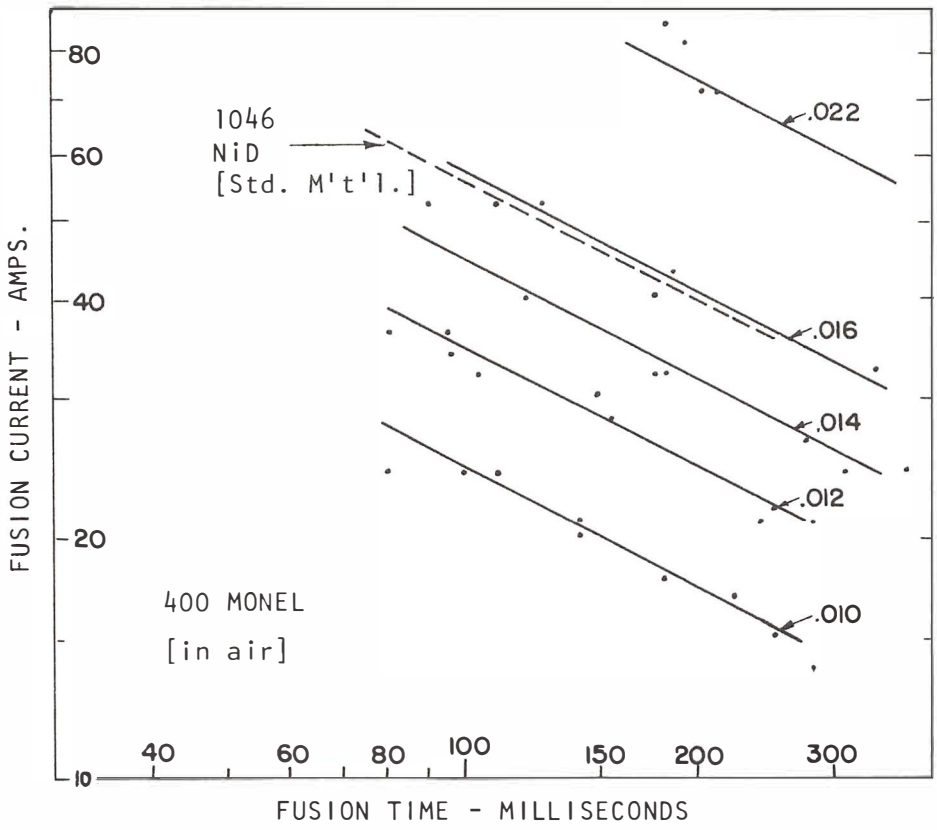


FIGURE 3 TYPICAL VARIATION OF FUSED CURRENT WITH FUSION TIME AND LEAD DIAMETER [400 MONEL]

TEST RESULTS

100 Watt	120 Volt	A-19	Incandescent Lamp
Standard Fuse	NiD	10 mil. diameter	

ALTERNATIVE FUSE

Nickel Plated Dumet 14 mils diameter with flat

The flat thickness should not exceed 3 mils.

Under normal conditions with no flat the I^2t difference between 10 mil N.D. and 14 mill NiPlated dumet would be:

Material	I^2t
N.D. 10 mil	61
NiPlated Dumet 14 mil	270

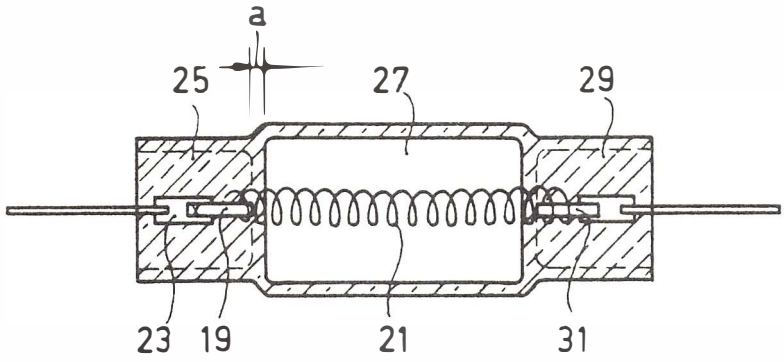
21.6 BASE ARC SUPPRESSION

When the fuse blows in the base, there are many factors which control whether the arc is extinguished or continues until the entire fuse lead or leads are consumed. One of the factors is the fuse material. For example, Nickel Plated Iron fuse leads result in more violent arcs than monel or NiD. The problem may be related to the carbon content of the iron.

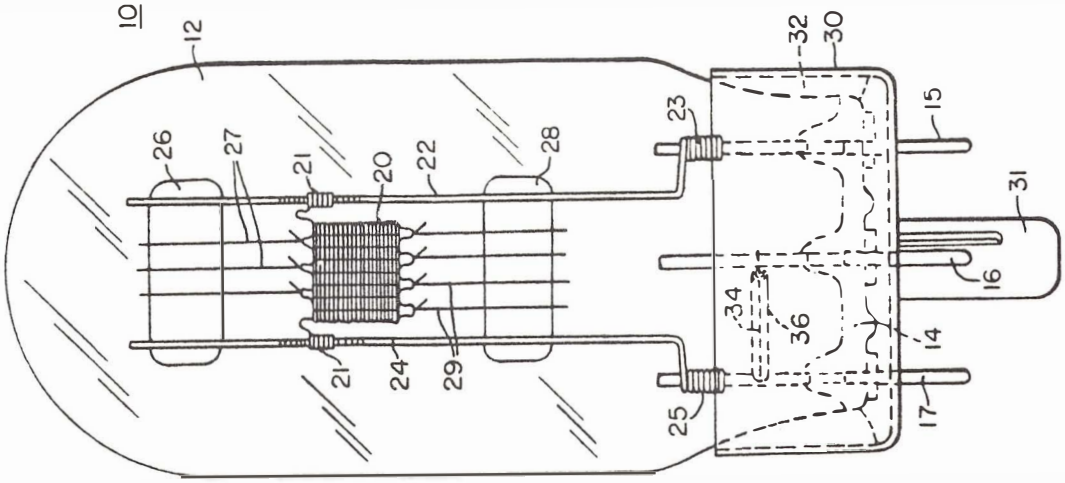
21.7 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

1. I^2t Lead Rating, by W.A. Anderson
GTE Sylvania, Danvers, Massachusetts - January 1977

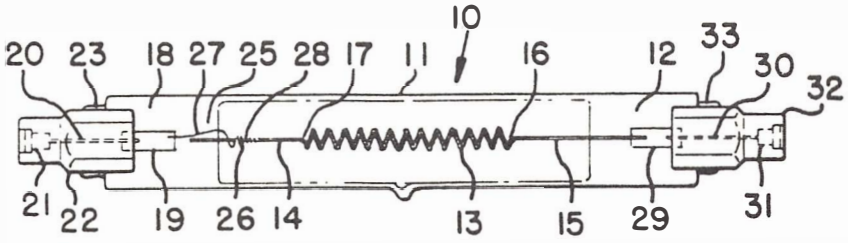
2. Halogen Filament Lamp Having an Internal ~~Arc~~ Protection Arrangement - U.S. Philips 1973
U.S. Patent #3,710,169



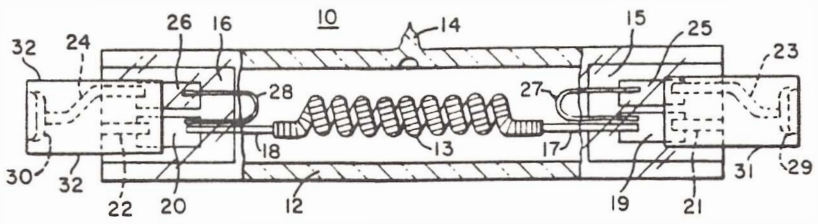
3. Halogen Cycle Incandescent Lamp Having a Platinized Interior Fuse
Westinghouse
U.S. Patent #3,727,091 (1973)



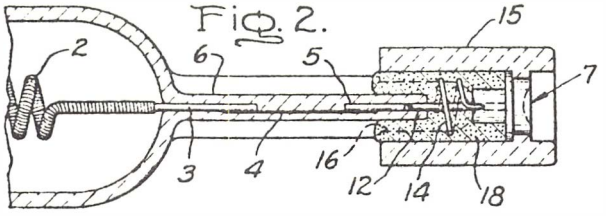
4. Incandescent Lamp with Internal Fuse
G.E. - U.S. Patent #3,864,598 (1975)



5. Gas Filled Incandescent Lamp with Integral Fuse Assembly
Westinghouse - U.S. Patent #3,132,922 (1979)



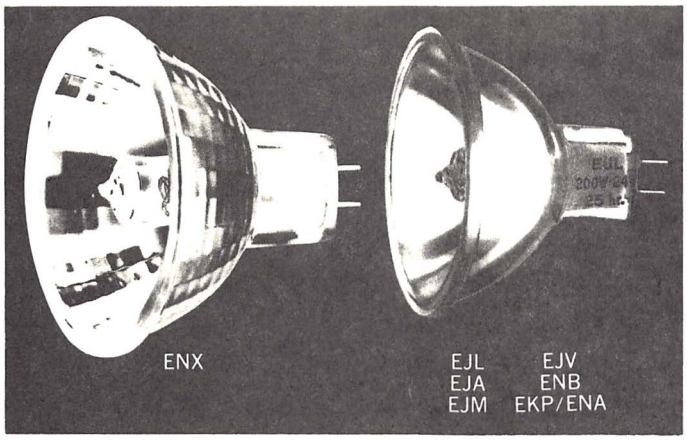
6. Incandescent Lamp with a Fuse Integral with the Lead-In Structure
G.E. - U.S. Patent #3,346,768 (1967)

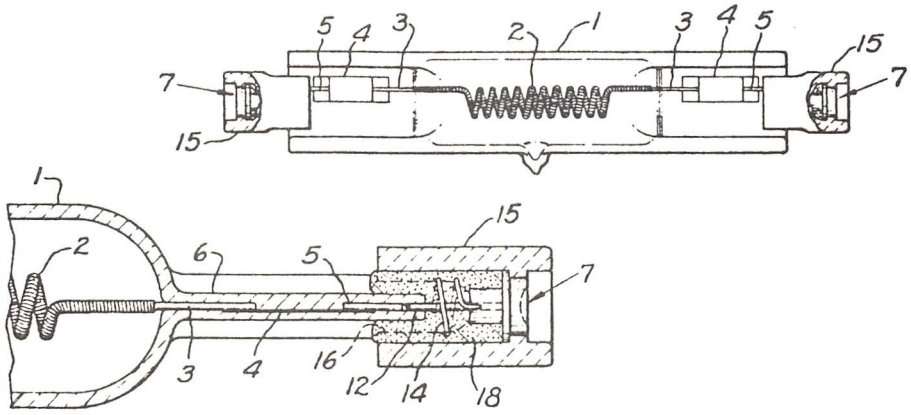


7. Incandescent Lamp Design and Manufacturing Handbook
by D.R. Dayton - GTE Sylvania

22.0 BASING CEMENTS

The base for some types of quartz halogen lamps are ceramics which are cemented to the press section of the lamp. Other lamps are cemented to a reflector -- that is the press section is cemented to an appendage at the apex of a reflector.





The temperature in the press - cement - base junction varies from about 350°C for long life lamps to approximately 550°C for high wattage short-life lamps in enclosed fixtures.

22.1 BASE CEMENT REQUIREMENTS

The requirements for the cement are:

a. Adhere to quartz and Ceramics.

b. Must not chemically attack the quartz.

c. Withstand operating temperatures for the life of the lamp.

d. Long pot. life.

e. Short cure time.

The cements are usually silicate such as Sodium Silicate or phosphates such as mono-magnesium phosphates. These materials do contain elements which will attack quartz under certain circumstances. The following table shows some of the reactions.

22.2 CHEMICAL BEHAVIOR OF FUSED SILICA ($\geq$ 99.8% SiO_2)

REAGENT	
Metals	**Reaction**
Ag.	No attack
Al.	Rapid attack at 700 - 800°
C	Reduction at 1050°
Ca.	In vacuum, up to dull red heat: none
Cd.	No effect; attack by vapor-phase material at elevated temps. over long periods.
Hg.	None, up to very high temps.
Li.	None up to 250°
Mg.	Rapid attack at 700 - 800°
Mn.	Attack only at high temps. in H_2
Na.	Attack by vapor-phase material at high temps.
P	Reaction
Pt.	Attack at high temps. in H_2
S	No appreciable attack
Sn.	None
Zn.	None
Metallic Oxides (1)	
BaO	Slight attack at 900°
CaO	Attack at 1000°
CuO	Attack above 960°
Fe oxides	None up to 960°
MgO	No appreciable attack

REAGENT	
Acids	
H_2O (even at 100°)	Virtually none
H_2SO_4	None
HNO_3	None
HCl (20°)	None
HCl (5%, 100°)	6 hr: 0.0005 mg/cm^2 loss
HF	Attack at all temps.
Phosphoric acid (300°)	Strong attack, though not so strong as on glass/ceramics

The effect of basing cement attack on quartz is to erode the quartz lamp wall until lamp fails. As expected different cements act differently.

22.3 BASING CEMENT TYPES

At this time it seems that Sauereisen #8 is a good compromise cement. When this cement is mixed properly and cured properly it is satisfactory for many applications.

G.E. 4-41 cement is extremely strong and has never shown ill effects on life in any application including the most severe problem areas. The cement requires 350°C curing temperature and is mixed with phosphoric acid.

G.E. CEMENT

(Typical - Not Necessarily #4-41)

USE

For basing lamps which require a high temperature cement.

PREPARATION

A. Formula

Material	Material Specification	Quantity
Disodium Phosphate, Anhydrous Powder	S020B	16 g.
Calcined Kaolin	PG51A	1.16 Kg.
Trialuminum Phosphate	AL15A	0.88 Kg.
Alumina A-1	AL12C	10.32 Kg.

B. Preparation

Grind the disodium phosphate in a mortar to remove clumps or agglomerates. Weigh all the above materials into a five gallon wide mouth bottle.

Place on rolls for one hour.

C. Packaging

In pint paint jars, 300 g in each.

D. Labeling

BASING CEMEMT POWDER
No.

Date Made_____Batch_____

(address)

The lamp factories mix the above dry powder with phosphoric acid - 85% strength - to obtain the desired consistency for use.

CEMEMT SUMMARY

For best results we probably should end up using about three different cements.

Capabilities with exacting controls will be required for all.

Sauereisen 8 needs tight controls on mixing procedures followed by close control on oven temperature, speed, fixture mass and cement mass in order that moisture is driven from the cement slowly without boiling and without crusting over the surface too quickly which results in "explosive" surface crumbling due to steam escaping from the uncured volume below it.

GE 4-41 needs flame curing capability for best results.

Dylon C10 has longer pot life than Sauereisen #8 plus same curing time and mixes with water. Strength is nearly as great as GE 4-41.

Much more life testing is required before approval for use in certain applications.

The same controls are needed for this cement as is for Sauereisen #8.

The majority of cements evaluated to date have a very harmful effect on the life of halogen lamps and shows little or no visible signs.

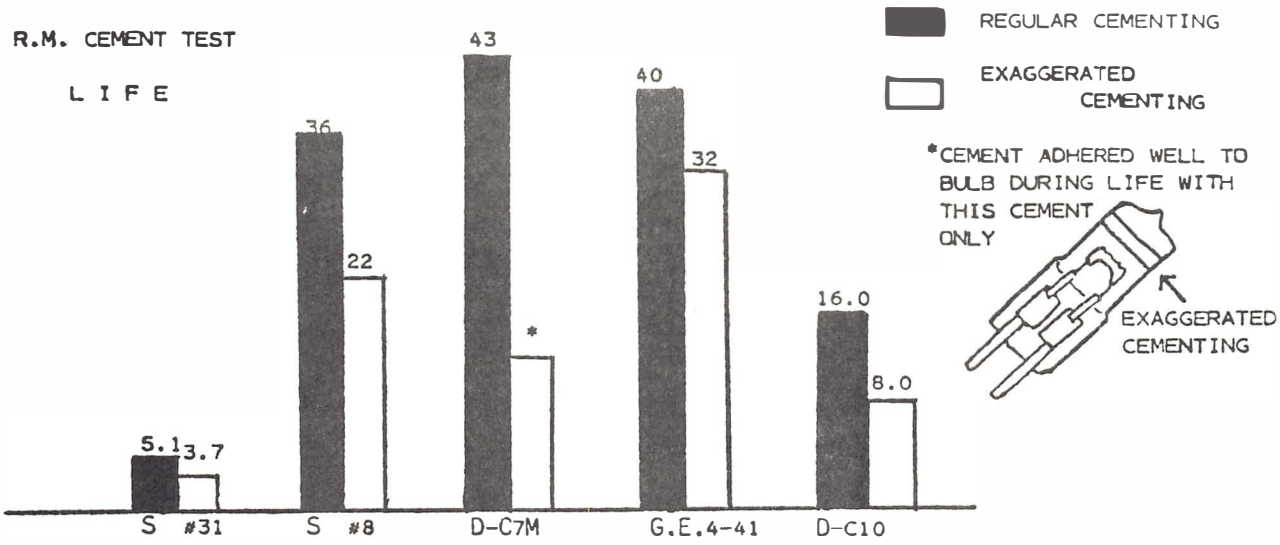
The most desirable cement from all standpoints (when properly controlled) is the Sauereisen #8, with water mix, relatively strong and very little effect on life.

Harmful effects cannot be predicted by the acidity of the cement.

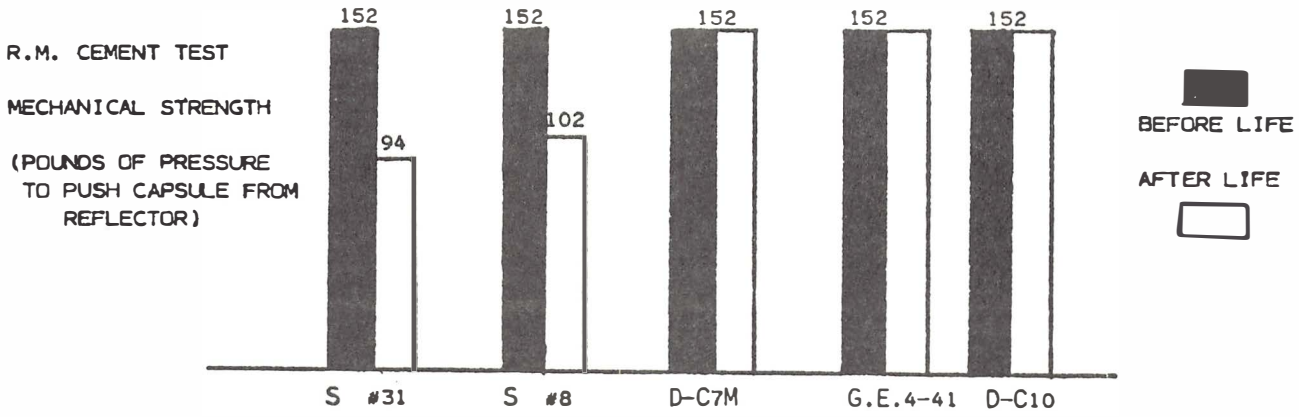
More than one type of cement must be used to cover all requirements.

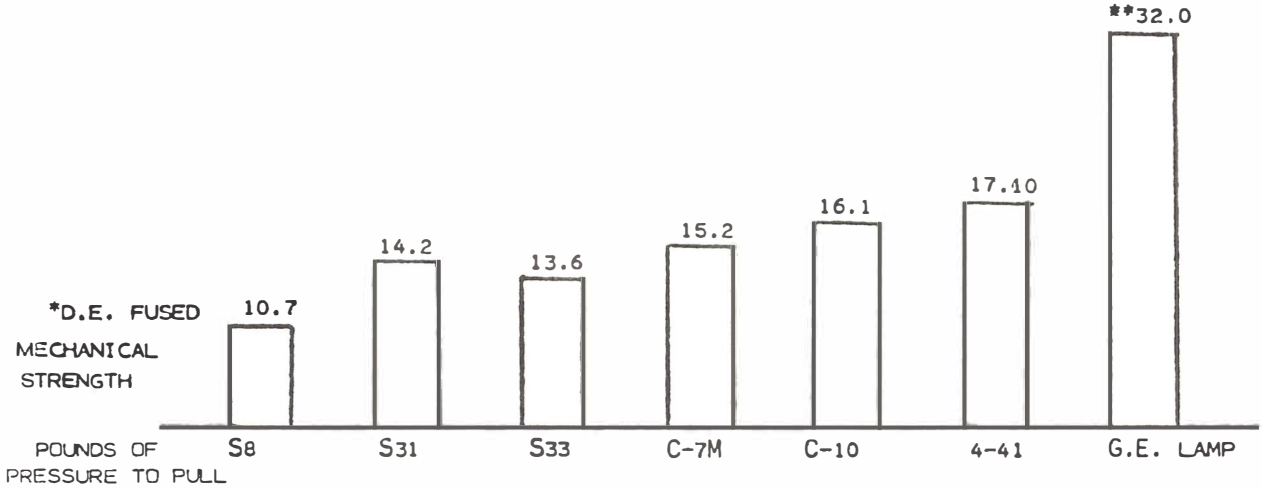
Several cements may be used selectively but must be evaluated for the particular application. Example: Dylon C10 is very strong and does not effect life on a 2000 hour 140 watt double end. However, when used on the ELH, life is reduced to 1/2 rated.

Sauereisen #31 most detrimental to life and unlike most of the cements evaluated, shows very extreme visible attack on the quartz.



* LIFE RESULTS NOT COMPLETE



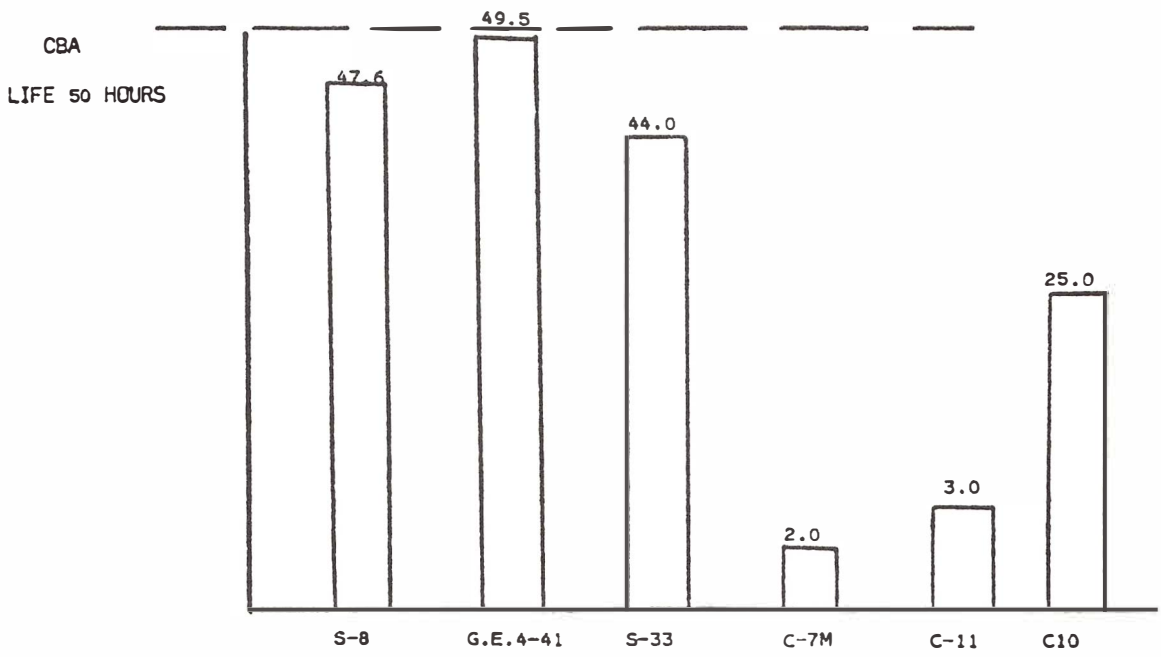


* D.E. FUSED TYPES ARE INHERENTLY WEAKER THAN NON-FUSED TYPES
* SYLVANIA CERAMIC SOMETIMES CRACKS GIVING POOR RESULTS

** G.E. PRESS BREAKS AT 32 POUNDS - BASE STRENGTH FAR EXCEES THIS
S33 HAS THE BASE ADHESION BUT POOR COHESION

C B A HEAT CAP

C E M E N T



S-8 REGULAR PRODUCTION-FIELD COMPLAINTS, LOOSE CAPS

G.E.4-41 VERY GOOD BOND - REQUIRES 350°C CURE

S33 GOOD BOND, SURFACE BLACKENS DURING LIFE

C7M TIP OF LAMP IS EATEN AWAY ON LIFE

C11 TIP OF LAMP IS EATEN AWAY ON LIFE

C10 GOOD BOND - NO VISABLE DETERIATION

CEMENT SUMMARY (continued)

Most critical lamp types for evaluation of cement have been the ELH and CBA heat cap.

All cements evaluated appear to be quite good heat conductors, i.e., ELH rim mount press temp. measurements.

Sauereisen #8 cement made using mono magnesium phosphate produced by Towanda has been stronger and more resistant to softening by H_2O than that using mono magnesium phosphate supplied by Ranson and Randolph.

Quality of the basing ceramic greatly effects the quality of the cement that comes in contact.

There is a two to one strength improvement on D.E. bases when cement is applied to lead-quartz-button first and ceramic then put in place versus the old technique of squirting cement through the ceramic clearance.

Quality of Sauereisen is improved by holding the amount of water to a minimum and curing temperature must be held below 100°C for initial curing of cement to prevent boiling which results in flaky cement.

22.4 BASING CEMENT TESTS

In studying an improved method of applying basing cement to double ended lamps, a method was devised to pull the base ceramic from the glass and record the pounds of pressure required, as a test of cementing techniques and cements.

In addition, water solubility tests and acidity tests were run on each cement tested.

For the strength tests to be meaningful, the basing technique used must be considered.

Using the new method now being developed provides much improved strength over the present method.

Example: Using Sauereisen 8 water mix.

NEW METHOD	PRESENT METHOD
40	9.0
30	18.0
21	4.0
38	13.0
37	11.0
$\bar{x}$ = 33.2 pound	$\bar{x}$ = 11.0 pound

CEMENT TEST UPDATE

Extensive testing of different type cement for base and heat cap application for CBA and other C-130 types shows no promising results due to attack on Vycor by the cement.

1. Dylon C-11 was tested with unsatisfactory results as the drying time of 3 hours was too long. After 2 hours burn time the cement attacked and destroyed the Vycor tip under the heat cap of CBA types.
2. Dylon C-7 was tested with the same results as Dylon C-11. The cement destroyed the tip after 3 hours burn time with heat cap on.
3. Thermostix #3000 mixed with potassium silica was tested with CBA heat caps. Results were unsatisfactory as the thermostix attacked the side of the Vycor bulb just under the heat cap edge after about 3 hours burn time.
4. Thermostix #3000 was also tested in the base of BVN (75QW 50 hour) lamps with fair results as there was no indication of any attack on the Vycor press after 78 & 93 hours burn time.
5. Thermostix #2000 was tested on CBA heat caps with unsatisfactory results as the thermostix attacked the Vycor just under the edge of the heat cap after about 4.3 hours burn time. This Thermostix #2000 was also mixed with potassium silica.
6. Fortafix (LQ/56) mixed with LQ/56 binder was tested on CBA heat cap application with unsatifactory results. One lamp with burn time of 43.2 hours showed attack on the Vycor under the heat cap. The other lamp showed some attack on the Vycor.

BASING CEMENT STRENGTH EVALUATION

The Following Data Show One Series of Cement Studies

CEMENT	Strength	Failure Mode	Color	Initial Cure Time	15 min	/ 24 hrs.	Acidity
AREMCO	34.0	Press	White	350°/10 min.	hard	hard	Basic PH10
GERMAN PHOSPHATE	25.0	Bond	White	250°/10 min.	hard	hard	Acid PH3
G.E. 4-41	35.0	Press	White	350°/10 min.	hard	hard	Acid PH3
Sauereisen #8	33.0	Bond	White	95°/7 min.	soft	very soft	Neutral PH7
#8X with #31 binder	34.0	Press	White	95°/7 min.	soft	very soft	Basic PH10
Sauereisen #31	20.0	Bond	Tan	95°/7 min.	hard	hard	Basic PH9
Sauereisen #12	28.0	Bond	White	95°/7 min.	soft	very soft	Acid PH9
#6 Towanda (New)	30.0	Press	Tan	95°/12 min.	hard	hard	Acid PH5
#8 R & R (New)	36.0	Press	Tan	95°/12 min.	soft	very soft	Acid PH5
Dylon C7	22.0	Cement	White	95°/7 min.	soft	very soft	Basic PH9
#8 with SILICATE OF SODA	15.0	Bond	White	95°/7 min.	OK	soft	Basic PH10

CEMENT TEST UPDATE (continued)

7. Sauereisen #31 mixed with #31 binder was tested on EPS 220 and 240V lamps with unsatisfactory results. The #31 attacks the press after about 5 to 10 hours burn time. BHC 120V was also tested with same results, #31 attacked the press.
8. Sauereisen #8X tested with unsatisfactory results. The mond-aluminum phosphate in Sauereisen #8X attacks the aluminum base destroying the color. #8X when used in CBA heat cap application is inadequate as after several hours burn time the cement expands causing a small crack in the tip and will not hold the heat cap on. As the heat cap pulls off, the tip comes off with the heat cap. This expansion will cause the heat cap to crack after about 25 hours burntime.

CEMENT TESTS

CEMENT	SET UP TIME **	PUSH STRENGTH *	COMMENTS
Sauereisen #8	1 hour	20-30 lbs.	Presently used
Sausereisen #8X	20 min.	70 +	Set up time too fast
Sauereisen #31	38 min.	70 +	Affects ELH life
German Phosphate	Oven only	100 lbs. +	Requires 2 hour oven bake
Dylon C-7	3-4 days	50 +	Requires oven or overnight air cure
Aremco 552	Pre-mixed	50 +	Attacks reflector glass

* AT END-OF-LIFE
** AFTER MIXING

The net result of present tests indicate that Sauereisen #8 is the best overall cement for most applications. It should be noted, however, that Sauereisen #8 is inconsistent in its mixture but this can be compensated by controlling the oven speed, temperature, and changing the formula to coincide with the incoming mixture for correct drying. Heat build up is the factor that causes violent reaction and attack on Vycor or quartz by the different cement types. Sauereisen #8 is not affected by the heat buildup.

23.0 HALOGEN LAMP OPERATING PARAMETERS

23.1 BURNING POSITION vs THERMAL SEPARATION OF GASES

Long Linear Iodine lamps are the most sensitive to burning position. Commercial lamp data state that lamp must be within 6 degrees of horizontal. Even one degree can be detected by noting color of iodine concentration at both ends of a lamp which has been energized for a few minutes and observed during cool down before the iodine condenses. It has been shown that the iodine operation is nearly the same for a 25 degree tilt or for 90 degrees (vertical Burning).

Lamp blacking at upper end of lamp occurs when the iodine concentration falls below the minimum required. A test lamp was made up for the purpose of determining the minimum amount of iodine required to clean up blackening. The lamp was blackened over its entire length by operating the filament at high temperatures in vacuum. The lamp was then given a dose of iodine plus iodine-131 and filled to 1760 Torr argon. It was then set burning vertically and the clean-up was observed. Clean-up occurred around all support wires first, and then the envelope sections between supports cleaned up gradually from the lower end of the lamp. The lamp was allowed to operate until no further clean-up was evident. The iodine concentration was then measured at the transition point, which was reasonably well-defined. It was found that approximately 0.001μ moles/cc of iodine were required for clean-up.

Figure 1 shows the separation of iodine in argon as a function of lamp fill pressure.

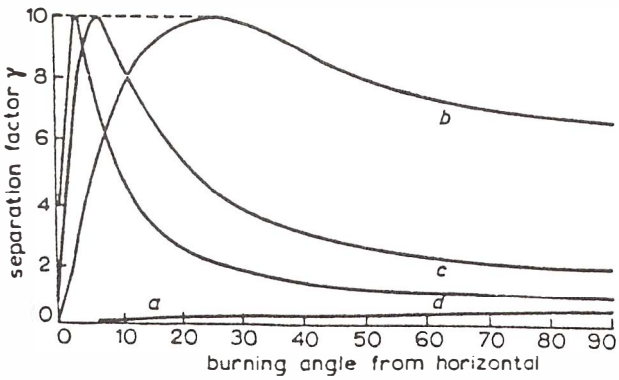


Figure 1
Separation of iodine in argon in 1 KW floodlight
a Pressure = 0.2 atm
b Pressure = 2.0 stm
c Pressure = 4.0 atm
d Pressure = 6.0 atm

Long life linear halogen lamps are primarily iodine dosed. The problem of halogen separation decreases with bromine.

Figure 2 shows the separations of bromine in Argon, Krypton and Xenon at 2 atmosphere fill pressure.

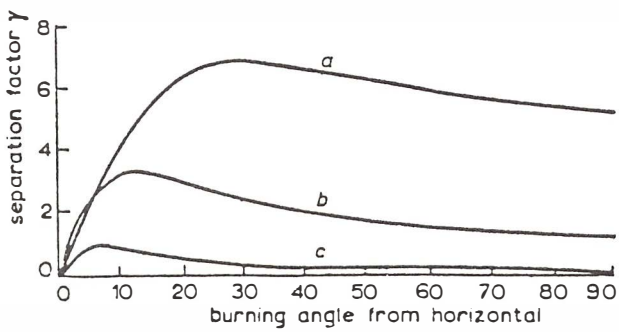


Figure 2
Separation of bromine in argon, krypton and xenon in 1 kW floodlight
a 2.0 atm, argon
b 2.0 atm, krypton
c 2.0 atm. xenon

The problem of separation occurs in all lamps to some degree. However, as long as the minimum dose required is available at all points the separation is not detected nor is it a lamp life determining factor. Table 1 shows that the best overall lamp fill would be Xenon and Bromine.

Table 1
THERMAL-DIFFUSION FACTOR FOR TYPICAL
TUNGSTEN-HALOGEN-LAMP FILLINGS

Filling gas and Halogen		Thermal-diffusion factor α
Ar/I_2	currently used	-0.716
Kr/I_2		-0.460
Xe/I_2		-0.265
Ar/Br_2		-0.488
Kr/Br_2		-0.240
Xe/Br_2		-0.073
Ar/Cl_2		-0.237
Kr/Cl_2		+0.028
Xe/Cl_2		+0.147

Notes: If $\alpha = 0$, there is no separation of halogen at any angle. The negative sign indicates that the halogen settles at the bottom of the lamp, and conversely if α is positive.

The coefficient α is slightly temperature-dependent, and an average value is given.

Note that Xe/Br_2 and Kr/Cl_2 look extremely favorable.

Separation of gases of different molecular weights does not occur when there is continued mixing of the gases due to convection and diffusion. One way to decrease separation in linear lamps would be to increase the bulb diameter to allow more convection.

There is some bulb length to diameter ratio which is acceptable and above this value separation will occur.

A study of Convection and Diffusion in halogen lamps has shown that universal burner lamps can be made with normal lamp dimensions if dead areas are eliminated.

23.1.1 Convection and Diffusion

Small size is a basic element of quartz halogen lamps. There are various shapes, from long thin double ended lamps (240 volts, 1500 watts T-3) to short fat single ended lamps (650 watt G7). The wattage varies from about 30 watts to 10,000 watts.

The ratio of convection to diffusion in a lamp varies with pressure, bulb size and coil temperature.

In general $\frac{\text{convection}}{\text{diffusion}}$ is proportional to $\frac{P^2R^3}{T^3}$

Where P = fill gas pressure
R = bulb radius
T = coil temperature.

Bulb radius is obviously a major factor.

Method of Study

Various bulb shapes have been contaminated with small amounts of air and then energized to oxidize the coils and to evaporate the tungsten oxide to deposit on the bulb wall. The tests are repeated base up, base down, base horizontal, etc. The smoke patterns are then compared for similarities, oddities, or whatever.

The results with a 1500 watt, 240 volt T-3 lamp are nearly the same regardless of the burning position. The only noticeable change is that the void area at each section is at the bottom, indicating that the evaporated tungsten moves radially from coil and slightly upward. In other words - mostly thermal diffusion and very slight convection. In one case a hole was cut in bulb below last section and lamp was lighted. Again no convection no chimney even with exhaust tube open.

A 600 Watt - 80 Volt - T-6 lamp was tested in the same manner as the 1500 Watt. A clear band around the bulb was evident and smoke deposited above the clear band by convection. The clear-smoke line is the boundary between diffusion and convection.

This lamp (BRT) has an unusual application problem. In use, one side of the bulb is air cooled with a blower. Some lamps turn black on the side opposite the air cooling. The only logical reason for the blackening is a lack of halogen on that side. The possible reason for this will be explained further on in this section.

The pattern of blackening on back side is same from lamp to lamp.

If a BRT lamp is cooled on one side while depositing tungsten oxide, the deposit takes the same geometry as the blackened side of the actual halogen lamp. The reason in this case is probably convection only.

23.1.2 Thermal Diffusion of Gases

When a linear iodine lamp is operated in a vertical position, two conditions take place. (1) The iodine settles to bottom of lamp. This can be seen after lamp has been turned off and started to cool. The iodine concentration is heavy in lower part of lamp and diminishes to near zero near middle of lamp. (2) An iodine lamp operated for a length of time in a position more than 4° off horizontal will blacken at higher end. The blackening will approach the middle area of lamp or below as lamp position approaches vertical burning.

Why does iodine settle to the bottom of lamp?

First of all, because there is little or no convection in lamp and second because the iodine vapor is heavier than the fill gas.

The following table shows molecular weight of various halogens and fill gases.

Halogen	Molecular Weight
I_2	253.8
Br_2	159.8
Cl_2	70.9
F	18.9
Fill Gas	
Nitrogen N_2	28.
Argon Ar	39.9
Krypton Kr	83.8
Xenon	131.3
Halogen Compounds	
HBr	80.9
HCl	36.46
HF	20.
HI	127.9
Metal Halides	
WBr_6	583.4
WCl_5	361.1
WF_6	297.8
WI_2	437.66

The table shows that after the halogen compound has dissociated, the halogen (I_2 or Br_2) is heavier than any of the fill gases. Before the lamp is energized, there is little or no separation because there is no thermal gradient. In other words, an iodine lamp will not separate just by holding it in a vertical position.

The table indicates that a lamp made with Cl_2 and Kr should reverse from the iodine lamp because the Krypton is heavier than chlorine. However, a lamp was burned vertical with Cl_2 and Kr and the results still indicated the halogen settled to bottom of lamp, probably because the Cl_2 disassociated to atomic Cl which is lighter than Krypton.

A review of theory of thermal-diffusion indicates that: If a temperature gradient is applied to a mixture of two gases, there is a tendency for the heavier molecular to move to the cold side and for the lighter molecular to move to the hot side.

Columns which have same properties as linear lamps have been used to separate Ar and He, Ne and H_2, N_2 and He, CO_2 and H_2, He and Br, even C^{13} and $C^{12}H_4$. The column used to separate $C^{13}H_4$ is 40 feet tall. The temperature gradient in the linear lamp is much greater than normal thermal diffusion columns.

Conclusion

1. All halogen lamps are subject to thermal diffusion and separation of gases to various degrees just like iodine lamps.
2. Even when separation takes place, there is a concentration gradient which is sufficient to supply the necessary halogen to a short filament so that lamps with short filaments can be burned in any position.

   For example, a T-3 lamp with a 1" filament might be universal burning and a 2" or more filament might be horizontal burning only. From 1" to 2" the burning position would be more horizontal as the filament gets longer.

WHAT CAN BE DONE TO GET BETTER DISTRIBUTION OF HALOGEN IN QUARTZ HALOGEN LAMPS?

It seems reasonable that if thermal diffusion and separation occur, that any gases which migrate below the boundary line or into clear area on lower end of linear lamp are lost to the lamp. Experimental lamps made wherein a long press iodine lamp was made such that the stagnent volume at both ends of the lamp were eliminated. The long press lamp was burned vertically and remained clean at both ends. Elimination of the stagnent volume kept the iodine from settling at lower end of lamp.

Figure 1 shows the conventional lamp on the left and long press lamp on the right.

IONAL IN-DEPTH INFORMATION

The lamps were burned in

The lamp with the long Pr

WHY DID COOLING OF ONE SI
OPPOSITE SIDE?

The answer is not clear,

1. The condition can be
2. Since lamp burns base
   tion, the concentrati
3. The blackening that c
   that localized area.
4. The cooling of one si
   terns on the other si

Conclusion

1. The cooling induced d
   increased halogen con
   lection of heavy halo
2. The fact that the BRT
   by condensing the met
   tends to keep the pro
3. The lamp would be impr

CONCLUSIONS FROM SMOKE STU

1. Thermal diffusion and
2. The halogen concentra
   of dead areas at both
3. Thermal gradients cau
   for gravity. Heavier
   more effective when w
4. A tapered bulb shape
   might have some inter
5. Lamp should have long
   which would cause sea

sion Separation in Regenerative Cycle Lamps
D. H. Green
971.

ır Tungsten Halogen Lamps

ol. 118 - No. 7 - 1971.

Linear Tungsten Halogen Lamps

ol. 119 - No. 12 - December 1972.

OF FILL PRESSURE

e, the higher the thermal conductivity of
s real, but the values are small. The fol-
ge in lumens for variation in fill pressure.

Lumens	Change
3250	
3200	-1.6%
3090	-5.2%
4800	--
4750	-1.0%
4590	-4.6%

the fill pressure by a factor of 4 only
proximately 5%.

FILL PRESSURE

data indicate that life varies directly with
his is only true when the mode of failure is
a direct result of filament temperature and
ects or fill gas contaminates such as O_2,

life vs fill pressure for 88/12 fill gas with
ife projection lamps.

Fill Pressure	Life Hours
1 ATM	6.
2	15.5
3	25.1
4	28.
5	37.4

The data show that life indeed varies with fill pressure, but life does not quite double when pressure is doubled. Computer analysis of data in Table shows that lamp life varies with fill pressure to the 0.895 power in this example.

23.4 LAMP LIFE AS A FUNCTION OF FILL PRESSURE AND HALOGEN DOSE

The following data show lamp life vs lamp fill pressure with variations in halogen dose for long life lamps.

A. LOW HALOGEN DOSE -- BLACK LAMPS

Fill Pressure	Lamp Life (Hours)
4	650
8	750
16	975

$$\text{Lamp Life} \propto \text{Fill Pressure}^{0.3}$$

B. NORMAL HALOGEN DOSE

Fill Pressure	Lamp Life (Hours)
4	680
8	1100
16	1600

$$\text{Lamp Life} \propto \text{Fill Pressure}^{0.62}$$

C. Above Normal Halogen Dose - Slight Attack at Cold Coil Ends

Lamp Fill Pressure	Lamp Life Hours
4	575
8	1090
16	1375

$$\text{Lamp Life} \propto \text{Fill Pressure}^{0.62}$$

D. High Halogen Dose - Cold Ends Heavily Attacked

Lamp Fill Pressure	Lamp Life Hours
4	450
8	600
16	750

$$\text{Lamp Life} \quad \alpha \quad \text{Fill Pressure}^{0.37}$$

In some cases of excess halogen, the entire filament will become faceted and look like hundreds of tiny mirrors. This is redeposited tungsten from evaporated W from hot part of filament in addition to redeposited W from cooler areas due to halogen attack.

The shorter the lamp life, the more likely the mode of failure will be evaporation. If the lamp in the preceeding data were run at a higher voltage, the results would be somewhat different.

The followng data is same type of lamp run at 115% rated volts.

A. Low - Low Halogen Dose - Black Lamps

Lamp Fill Pressure	Lamp Life Hours
4 ATM	140
8 ATM	190
16 ATM	220

Conclusions

1. The data show that lower pressure lamps which blacken due to low halogen dose have longer lives than lamps with higher halogen dose and remain clean. This fact indicates that lamp life is affected by halogen attack of the filament.
2. The data show that higher pressure lamps which blacken due to low halogen have shorter lives than lamps which have higher dose and remain clean. The reason is obscure, but probably relates to more diffusion, less convection and higher bulb wall temperatures.
3. The halogen dose is more critical for long life lamps than short life lamps.

23.4.1 References for Additional In-Depth Information

1. Life and Luminous Flux of Halogen Incandescent Lamps Related to Filament Temperature, Pressure and CH_2Br_2 Content, by J.R. de Bie and J. C. M. A. Ponsioen.
Lighting Research and Technology, Vol. 9, No. 3 - 1977.

23.5 MEASUREMENT OF INTERNAL LAMP PRESSURE

23.5.1 COLD PRESSURE - BELOW ATMOSPHERIC PRESSURE

23.5.1.1 Water Method

The usual method is to break the tip while the entire lamp is immerged in water. The lower the pressure, the more water will enter the lamp. The actual pressure can be measured or calculated by several means. One simple way is to weigh the lamp before breaking tip, weigh the lamp again after inhalation of water and then fill the lamp completely with water and weigh again.

Bulb plus 100% filled with water = X

Bulb plus partial fill with water = Y

Bulb weighed before test = Z

X - Z = Total water weight

Y - Z = Partial Fill water weight

$$\frac{Y - Z}{X - Z} \times 760 = \text{fill pressure in Torr}$$

If the internal volume of the lamp is known, the fill pressure can be calculated by measuring the weight of the bulb before and after breaking tip under water.

Y - Z = weight of water in bulb in grams

1 cc of water weight 1 gram

Lamp volume cc times 1 gram = Weight of total fill with water.

$$\frac{Y - Z}{\text{Bulb Volume}} \times 760 = \text{Fill pressure in Torr}$$

Alternate Water Method

I. Gas Pressure by Water Method

This method involves breaking the seal of the lamp under water and allowing the water to be sucked into the lamp up to atmospheric pressure. This water is measured for volume, and the total volume of the lamp is also measured. The difference between these two volumes is the volume of contained gas at atmospheric pressure and the temperature of the water. The original pressure of gas within the lamp is them computed, it being equivalent in percent atmospheres to the ratio of the volume of the gas as above measured to the total volume of the lamp.

II. Procedure

Remove the base from the lamp and submerge lamp completed in a bucket of water, the temperature of the water being regulated between 20° and 22° C (68° and 72°F). Invert the lamp under water to completely fill the stem tube with water, and break off the tip with the fingers. Allow the water to suck in, letting the lamp float base down. When no more water flows in, keep the lamp in a base down position and raise the lamp until the water level inside the lamp is the same as the level of the water in the bucket. Close the stem tube off with the finger and remove lamp from water, inverting it to a base up position to retain all of the water.

Break off the whole stem tube and measure the water in a graduate. Unless the total volume of the lamp is already

known, refill the lamp with water, leaving the broken mount inside the lamp (and thus refilling the stem tube as before) and measure this volume of water as before. A barometer reading should be made, and the pressure of the lamp computed by the following formula:

$$P = \frac{T-W}{T} \times B$$

Where P = the absolute pressure in mm of the gas in the lamp

T = total volume of lamp

W = volume of water sucked in

B = barometer reading in mm.

23.5.1.2 Weight Method

It is possible to determine the fill pressure in a lamp by measuring the weight of the fill gas.

A. Non-destructive

1. Measure weight of bulb and exhaust tube before exhaust.
2. Measure weight of tipped lamp and severed exhaust tube after exhaust and fill.
3. Subtract bulb and exhaust tip weight.

   1 - 2 = X

If X is positive the fill pressure is above atmosphere. For example, a 2.5 ml bulb filled to 5 atmospheres of Krypton, the fill gas weight can be calculated.

The following table shows the weight in milligrams/ml for common fill gases.

FILL GAS	WEIGHT
Nitrogen	1.1849738 mg/ml
Argon	1.6910691
Hydrogen	0.0851662
Krypton	3.5463435
Xenon	5.5878806

Therefore, 2.5 ml x 3.5463436 X 5 = 44.329295 mg.

With laboratory balances and a digital readout, this is not a difficult measurement.

B. Destructive

1. Weigh complete lamp
2. Break tip, save all fragments and reweigh lamp.
3. Measure lamp volume by filling with water after weighing.
4. Subtract (1) from (2) and calculate fill gas pressure.

23.5.2 ABOVE ATMOSPHERIC PRESSURE

The usual method is break the tip under water and capture the gas which escapes. This can be done by filling a funnel mouth graduate with water and then holding it upside down in a tub of water. The water level at top of graduate should be 100% - no air bubble. The tip of lamp is held below the graduate mouth and tip broken with a pair of hand cutters. The excess gas will rise to top of graduate and displace the water. The final level of water in graduate is then recorded. It is necessary to know the internal volume of the lamp. A simple method is to use a graduated syringe and fill the lamp with water after the lamp has been removed from water both with severed tip.

Lamp volume = X cc

Water displaced in graduate = Y cc

$\frac{Y}{X}$ = atmospheres over 1 atmosphere

Lamp fill pressure = $\frac{Y}{X}$ + 1 atmosphere.

Another method is to use a reference chamber of known pressure and volume. The procedure requires breaking the lamp after inserting it in or connecting it to the reference chamber. For this process the volume of the sample is also needed. This value can be obtained by immerging the lamp in a graduate and measuring the displacement or more accurately by filling a sample lamp with water with a graduated syringe.

P_1 = Reference Chamber Pressure

V_1 = Reference Chamber Volume

L = Lamp Volume

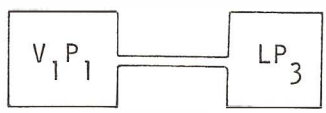
P_2 = Measured Pressure after breaking lamp in reference volume

P_3 = Lamp fill pressure

$$(V_1 - L) \cdot P_1 + L \cdot P_3 = V_1 P_2$$

$$P_3 = \frac{V_1 P_2 [(V_1 - 1) \cdot P_1]}{L}$$

If lamp is connected to a reference volume the calculation is different.



$$= (V_1 + L) \cdot P_2$$

$$V_1 P_1 + LP_3 = [(V_1 + L) \cdot P_2]$$

$$P_3 = \frac{[(V_1 + L) P_2] - V_1 P_1}{L}$$

23.5.2.1 X-Ray Intensity of the Krypton Filler Gas

A non-destructive lamp pressure test is desirable. Such a test could be used to sort out lamps which are below the required pressure.

Essentially, the method consists of exciting the krypton fill gas in the halogen lamps with polychromic X-rays. The krypton then emits Kr Kx characteristic radiation. The Kr Kx intensity is measured and related to the pressure in the envelope. The experimental work showed that there is direct correlation between Kr Kx intensity and measured gas pressure. In practice bulb glass composition, thickness and fill gas contaminates influence the measurements. The work was done by Lasar Analytics, Inc., Lexington, Massachusetts.

23.5.3 HOT PRESSURE - OPERATING LAMP PRESSURE

23.5.3.1 Molten Tin Method

The internal pressure in a lamp rises due to heating of the fill gas.

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

Where Pressure and Temperature are absolute values.

Measurement of the gas pressure at operating temperature is difficult because the high gas temperatures. One method which has been used successfully is the molten Tin plug. Figure I shows the apparatus. The process is to melt the tin so that it fills the bore of the exhaust tube and can be moved towards the lamp by pressure on head side of plug or towards the head by raising pressure in the lamp. When the pressure is balanced the plug is stationary and the pressure in lamp is equal to balancing pressure at head.

Figure II is a graph of the change in lamp pressure as a function of a change in lamp input voltage. The lamp was initially filled with 50% N_2 and 50% Argon at 3 1/3 atmospheres (49.86 psia). The pressure in lamp at 120 volts is 230 psia.

Computer analysis of the data in Figure II shows that the lamp pressure varies exponentially with input voltage.

$$\text{Lamp Pressure} \propto \text{Lamp Volts}^{0.425}$$

23.5.3.2 Lamp Current Method

It has been reported that hot fill pressure can be evaluated by measuring the lamp current at a know pressure and comparing the value against a similar unknown pressure lamp. Several tests have been made by Sylvania. The results indicate that this method of pressure evaluation is not reliable.

APPARATUS FOR DETERMINING OPERATING LAMP PRESSURES

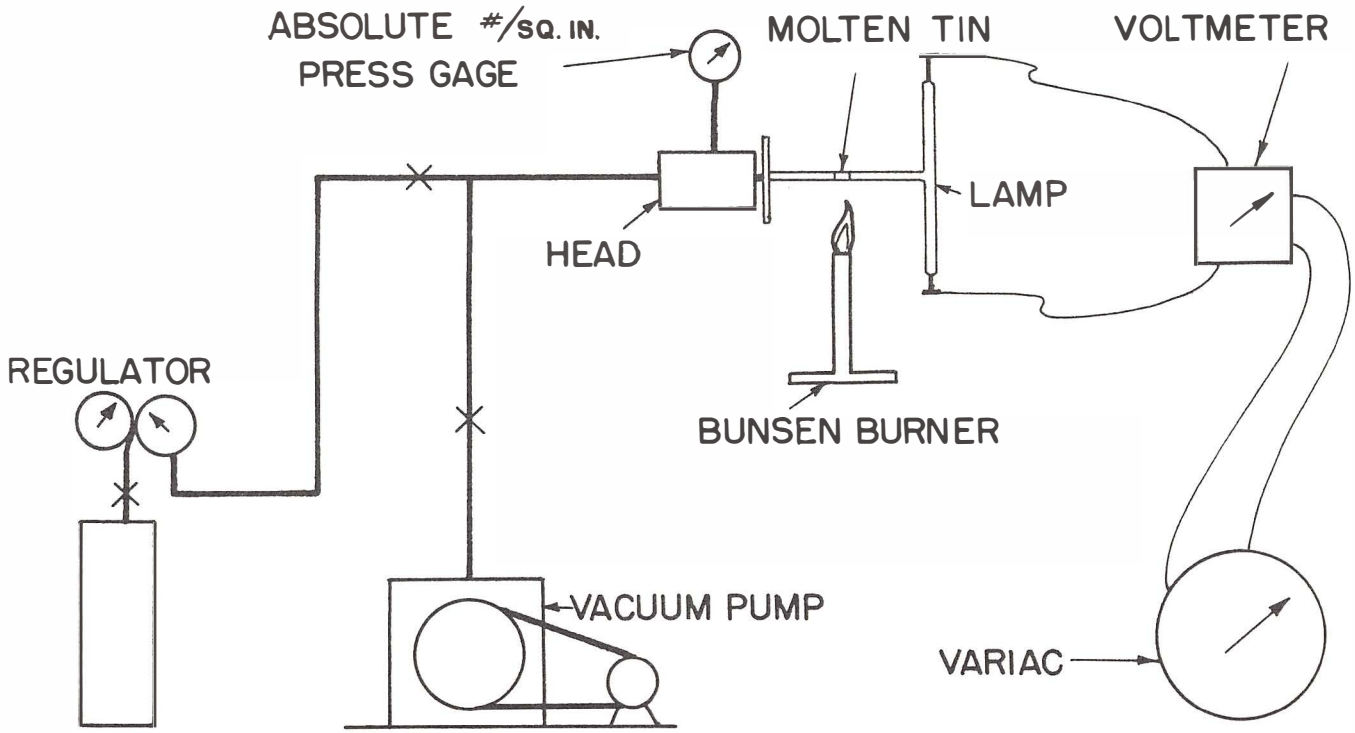
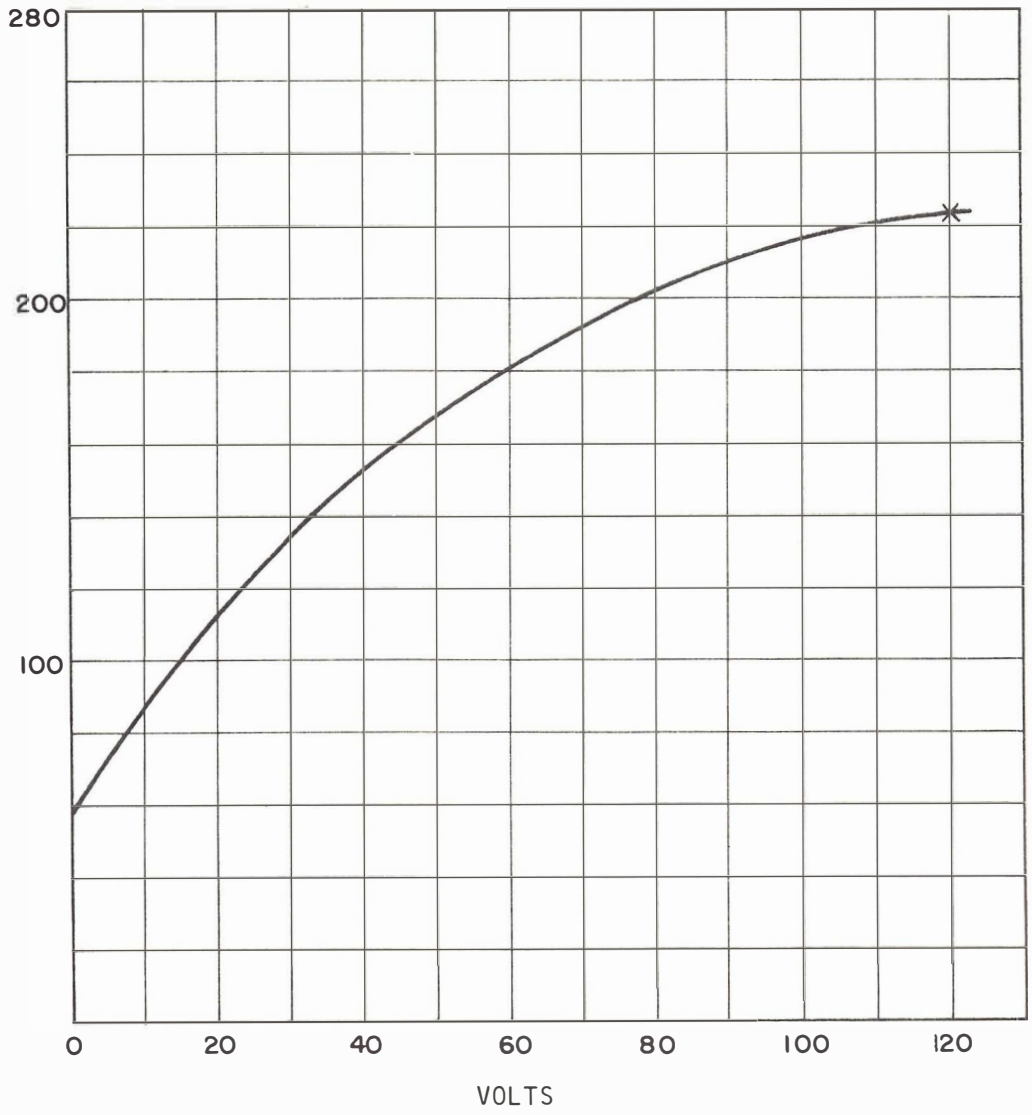


FIGURE I

FIGURE 11



FEY - COLD FILL PRESSURE
50# ABSOLUTE

The following table shows the change in lumens as a function of pressure for a test lamp.

Fill Pressure	Measured Lumens
4 ATM	4810
8 ATM	4750
16 ATM	4590

At constant voltage lumens change with current to the 6.25 power.

For a 400% change in fill pressure, the lumens changed 4.79% which would represent a current change of only 0.75%. This is too small a change to be of value to measure pressure to approximately $\pm$ 1/2 atmosphere.

23.5.4 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

1. Operating Pressure of Incandescent and Tungsten Halogen Lamps and Influence of Envelope Temperature on Life, by J.R. Coaton, Lighting Research and Technology, Vol. 9, No. 1 - 1977.

2. The Optimum Operating Gas Pressure of Incandescent Tungsten Filament Lamps by J.R. Coaton, Lighting Research and Technology, Vol. 1, No. 2 - 1969.

23.6 DETERMINATION AND MEASUREMENT OF HALOGEN DOSE

The specification for the halogen dose is usually arrived at by trial and error for a particular lamp type to reach a balance between lumen maintenance and lamp life. It is generally accepted that the higher the partial pressure of bromine, the less problem with black lamps and at the same time, the halogen dose has a negative effect on lamp life. For long life lamps, the halogen dose is important. For short life photographic lamps there is a great deal of flexibility in choice of halogen and concentration in fill gas.

For example:

DVY Sun Gun Lamp 650 Watt - 120 Volt - G-6

This lamp has a rated life of 25 hours. The halogen dose is usually HBr. Because of arcing problems, the HBr was increased to 10% (GE) in order to use HBr as an arc suppressant as well as the transport halogen

source. The high HBr level resulted in attack of cool ends of filament. The first turns after the insert are subjected to a great temperature gradient and are most rapidly attacked. GE added a loose fitting insert which resulted in a more smooth temperature gradient.

GE and Sylvania have produced other lamps with high HBr doses.

DYJ	-	5% HBr	
DAP	-	2% HBr	
DXW	-	2% HBr	150 hour life
BRH	-	2% HBr	75 hour life.

In general, the halogen dose should be no higher than necessary to achieve consistently clean lamps - but there are exceptions.

Measurement of the Bromine or Iodine Dose

The iodine dose is judged by color. This is not possible with bromine. The partial pressure of bromine in the tank when mixed is known. However, beginning with the tank and all the way to the lamp, bromine can by lost by chemically combining with metals, moisture, oil, etc., thereby reducing the halogen concentration in the fill gas that reaches the lamp. There are no known ways of determining the actual amount of bromine in a finished lamp. However there is one method which yields repeatable reference data.

23.6.1 Ion Selective Electrode for HBr Analysis

The lamps are placed in a clean steel cylinder and rinsed "in place" by several deionized water flushings. Fifteen mls. of deionized water is added and the lid put in place on the steel cylinder. The lamps are broken by a pistonlike ram which is part of the lid. The solution is then transferred to a 25 ml volumetric flask with rinsing of the cylinder and glass pieces diluted to volume and mixed by inversion. The concentration of the solution is then determined by comparing it to standard bromine solution using the Orion Specific Ion Method, as described in the Orion Procedure Manuals. In each case, as a check, the solution is subsequently titrated potentionmetrically for bromide.

The procedure is rapid and simple and is outlined here only briefly.

Calculation

$$\frac{\text{moles}}{\text{liter}} \text{ (from meter) } X\ 8.0\ X\ 10^{7}\ \frac{g}{\text{mole}}\ X\ \frac{1}{40}\ \text{liter} \div \text{no. of lamps} = \frac{\mu g}{\text{bulb}}$$

On the basis of tests, it seems quite feasible that the Orion specific ion method for determining bromide concentration (i.e., HBr) could be used. Initially, it would be used to check changes from one production date to another production date. However, with very little more effort, i.e., making up of known standards and interrelating them to the titrimetric values, absolute data are quite possible.

Looking at the data obtained on the various lamps, it must be noted that the HBr variation from lamp to lamp is much greater than the variation of a known solution by either method, indicating strongly a variation of HBr fill from lamp to lamp.

More complete data on this process can be obtained from James Keenan GTE Sylvania, Boston Street, Salem, Massachusetts, or from the GTE Sylvania Technical Assistance Group at the Lighting Center, Danvers, Massachusetts.

In addition to the Orion method, some work with laser absorbtion has been done by Laser Analytics, Inc., Lexington, Massachusetts. The laser method also yields the fill pressure. The major asset of the laser method is that it is non-destructive.

23.6.2 REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

1. Method of Dosing an Incandescent Lamp with a Controlled Amount of Halogen-Containing Material. Westinghouse. U.S. Patent #3,788,725 (1974).

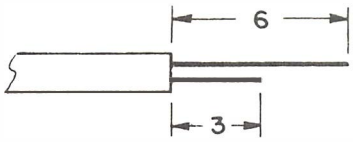
23.7 MEASUREMENT OF PRESS SEAL TEMPERATURE

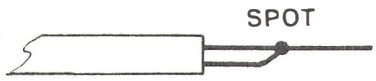
Order the desired lamps without bases from the appropriate manufacturing area. Recessed single contact type should have the silver plated contacts welded on.

Have a .025"-.030" hole drilled in the lamp seal by the Ultrasonic Drill.

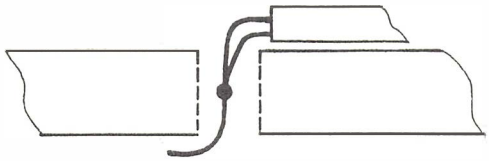
Order from the Clark H. Joy Co. 30405-T Clemens Road, Bay Village, Ohio 30 gage duplex glass braid insulated Iron Constantan Thermocouple Wire.

Cut the wire in 10" lengths. Strip off insulation from one end, so that 3 mm of one wire lead and 6 mm of the other wire lead are bare. Weld as follows:





Clean out drilled hole by running an alcohol moistened string through it. Insert thermocouple as shown.



Base lamps with care to maintain thermocouple location. On recessed single contact type, bend thermocouple wire on opposite side of the silver plated contact and roll up in a 2 1/4" diameter roll. Attach to the center of the lamp during the basing operation, with small soft bare cut wire.

Place lamps in a test fixture operated at rated voltage. Approximately one hour will be required for temperature stabilization. LAMP SEAL TEMPERATURE Readings should be as follows:

INFRARED

1000W T3 - Limits 320°C to 360°C

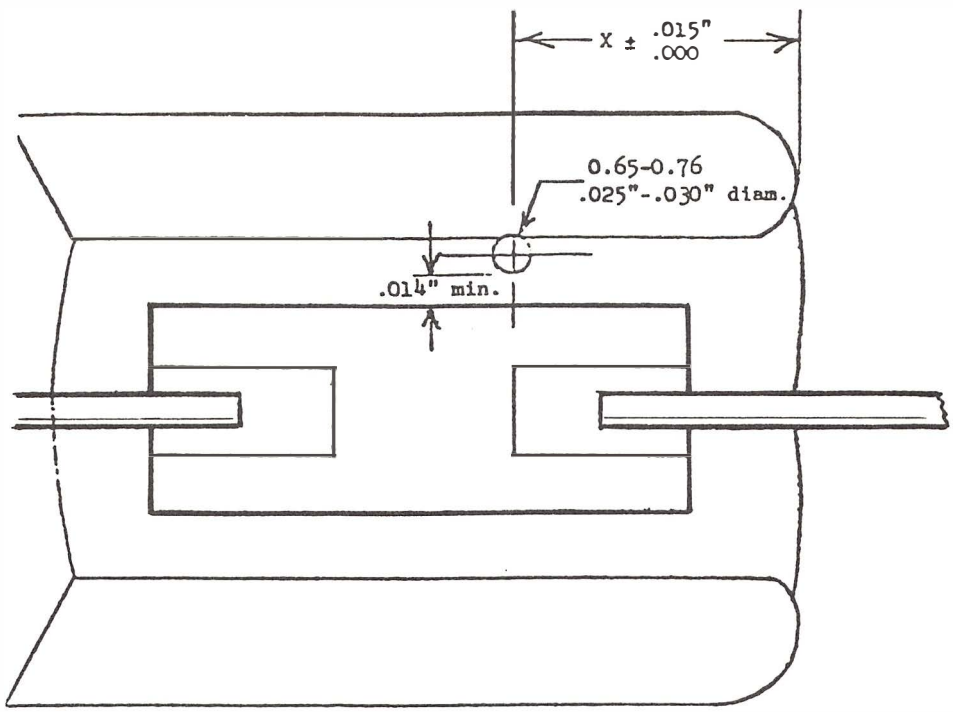
1600W T3 - Limits 330°C to 370°C

QUARTZ IODINE

500W T3 - 120V Use Appleton Quartz Lite Fixture No. G-6000 aimed 45° downward in still air. Limits 320°C to 355°C.

1500W T3 - 240V Use Wide Lite Corp. Limitor Fixture No. L-1500-B aimed 5" downward in still air. Limits 340°C to 375°C.

FOIL LEAD SEAL



Examine lamp and use side of seal which is largest. Drill hole at edge of rail as shown in sketch. There should be a minimum of .014" from the edge of the foil to the edge of the hole. Dimension (X) distance from sealed edge of the lamp to inner edge of the weld tab.

Dimensions for Ultrasonic Drilled Hole for Themocouple.

Drill one end only.

24.0 THE BURNOUT MECHANISM OF HIGH PRESSURE HALOGEN LAMPS

The mechanism for burnout of halogen lamps is somewhat different from that of general service incandescent lamps.

24.1 THEORY OF LAMP LIFE

The exponent "d" is defined by the equation

$$\frac{\text{Life}}{\text{LIFE}} = \left(\frac{\text{VOLTS}}{\text{Volts}}\right)^{d} \qquad (1)$$

or by $\quad "d" = -\dfrac{d(\log \text{life})}{d(\log \text{volts})} = -\dfrac{d(\ln \text{life})}{d(\ln \text{volts})}$

where it does not matter whether common or natural logarithms are used for the logarithmic derivatives.

The actual cause of the end of life in what might be considered "normal burn-out," that is in the case where life is not determined by some lamp defect such as sag, brittle filaments, or impurities in the gas, is some mechanism involving a specific amount of a physical processes having occurred. The critical assumption, therefore, is that the life is <u>inversely</u> proportional to the rate at which the process occurs. Thus

$$\text{life} = \frac{(\text{constant})}{\text{process rate}}$$

or $\quad \log \text{life} = -\log \text{rate} + (\text{constant})$

The rate of most physical processes depend very strongly on the temperature. Thus the temperature can be considered as being the variable which determines lamp life. Since the temperatures of a filament depends on the applied voltage.

$$"d" = -\frac{d(\log \text{life})}{d(\log \text{volts})} = +\frac{d(\log \text{rate})}{d(\log \text{volts})}$$

$$\text{and hence} \quad "d" = -\frac{d(\log \text{rate})}{d(\log \text{temp.})} \div \frac{d(\log \text{volts})}{d(\log \text{temp.})} \qquad (2)$$

$$\text{or} \quad "d" = \frac{d(\log \text{rate})}{d(\log \text{temp.})} \times \frac{d(\log \text{temp})}{d(\log \text{volts})}$$

It must be emphasized that this analysis does not say anything about the actual values of life but only the way in which the life varies with temperature or voltage.

24.2 THE ARRHENIUS EQUATION

The temperature dependence of the rates of many processes, such as chemical reactions and transport phenomena such as diffusion or evaporation, is given by the Arrhenius equation.

$$P = P_o e^{-Q/RT} \qquad (3)$$

Where P is the rate of the process, P_o is a constant independent of temperature, R is the universal gas constant (=2 kcal/mol/deg°) and T is the absolute temperature. Q is a constant called the activation energy of the process and is customarily given in calories per mole. Table I gives the activation energies of some pertinent processes of tungsten.

TABLE I

Tungsten Activation Energies

Process	Q(cal/mole)
Evaporation	208,500
Volume self-diffusion	135,800
Grain boundary self-diffusion	72,000
Void formation	98,000

An even more important indication that a process other than evaporation is responsible for the burn-out of high pressure lamps, at pressures above the point where the life is pressure dependent, is the fact that data indicate that the life exponent "d" has the value 7.8 in this region. This compares to the normal values of "d" of 12 or 13 for ordinary gas-filled incandescent lamps. Equation (3) indicates that a process with a lower activation energy Q would give a lower value for "d." The following section shows what may be learned from an analysis of the data.

ANALYSIS OF DATA

Consider the following experimental lamp.

Nominal volts	120 volts
Nominal watts	500 watts
Nominal efficiency	21 lumens per watt
Coil length	77 mm
Bulb	T-4, 8 mm I.D., 2 mm wall
Iodine	2.5 micromoles
Fill pressure	7100 mm Xenon

Table II gives the characteristics and Table II A the corresponding logarithms.

TABLE II

Lamp Characteristics

Volts	Efficiency	Temperature	Life
120	21 lpw	2945 °K	6000 hrs.
160	32	3288	600
188	40	3500	180

TABLE IIA

Volts	Log Volts	Log Temp.	Log Life
120	2.079	3.469	3.778
160	2.204	3.517	2.778
188	2.274	3.544	2.555

From these data we can obtain the life exponent "d" (Figure 3). Figure 5 gives the calculated exponents as a function of temperature, and also shows the value of "d" obtained from the data on high-pressure lamps.

On the basis of the activation energy for evaporation, the change should be about 0.5 in "d." Thus the "d" value is more nearly constant than theory would predict. Both of these observations can be explained on the basis that although the major position of the temperature dependence of life is accounted for by the exponential term in the Arrhenius equation, there will be some effect of temperature on the fine details of the process which determines the coefficient P_o. Thus we need not be overly concerned with the fact that the "d" observed for the high-pressure lamps appear to be constant independent of temperature.

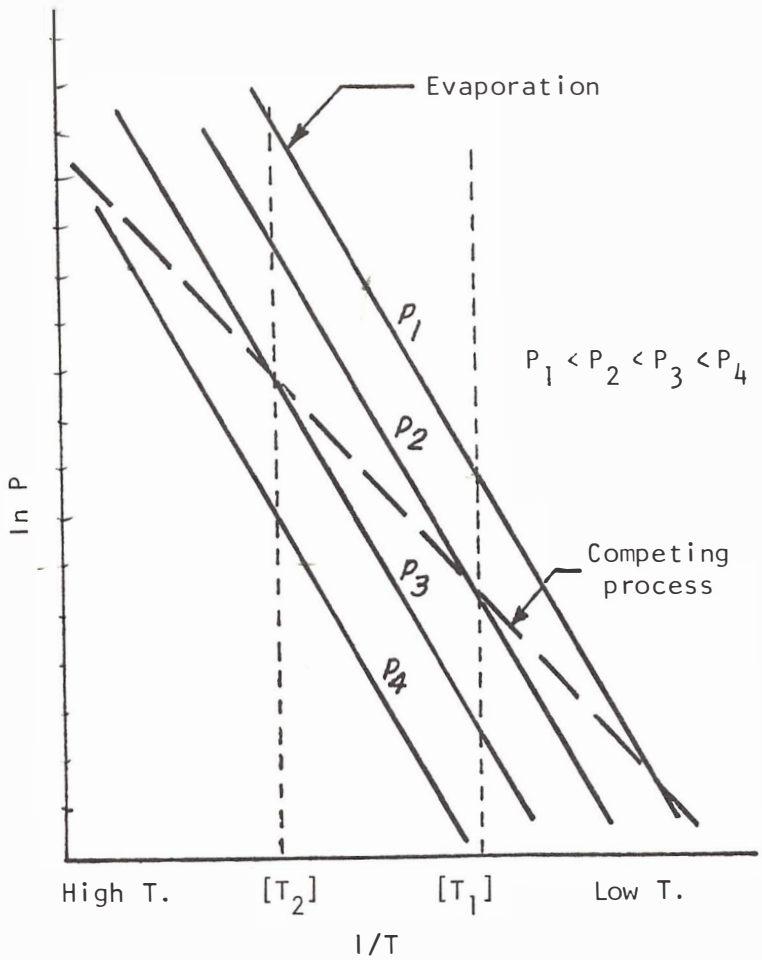


FIGURE 1

TEMPERATURE VARIATION OF RATE PROCESS

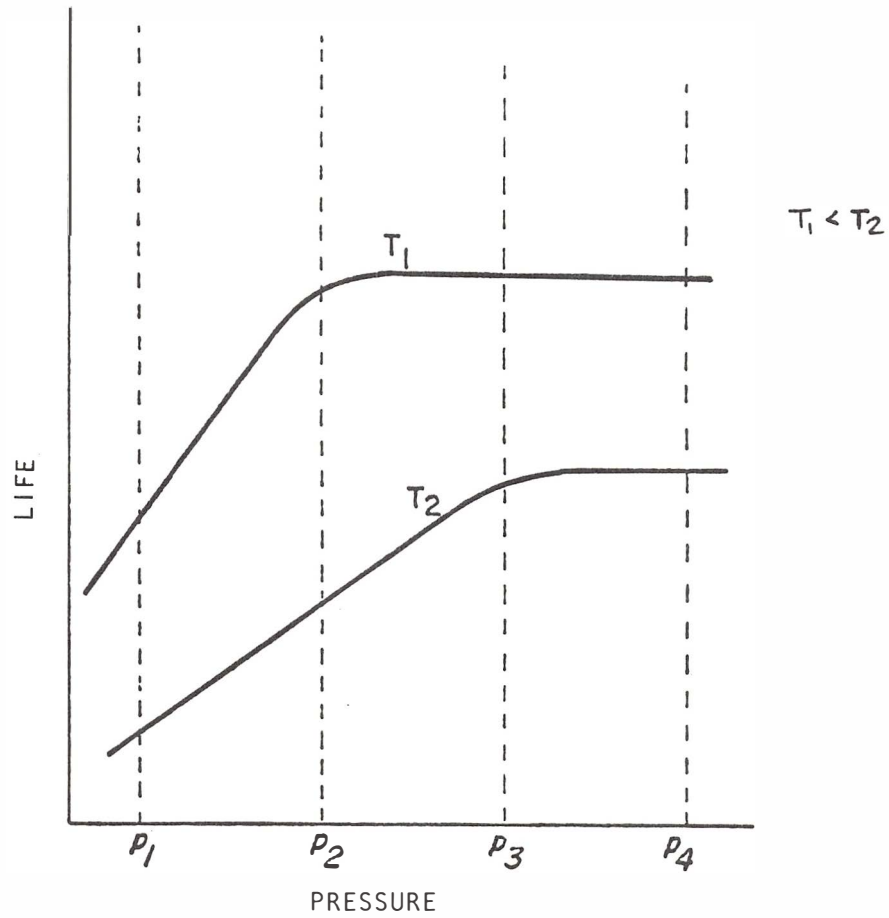


FIGURE 2

EFFECT OF PRESSURE ON LAMP LIFE

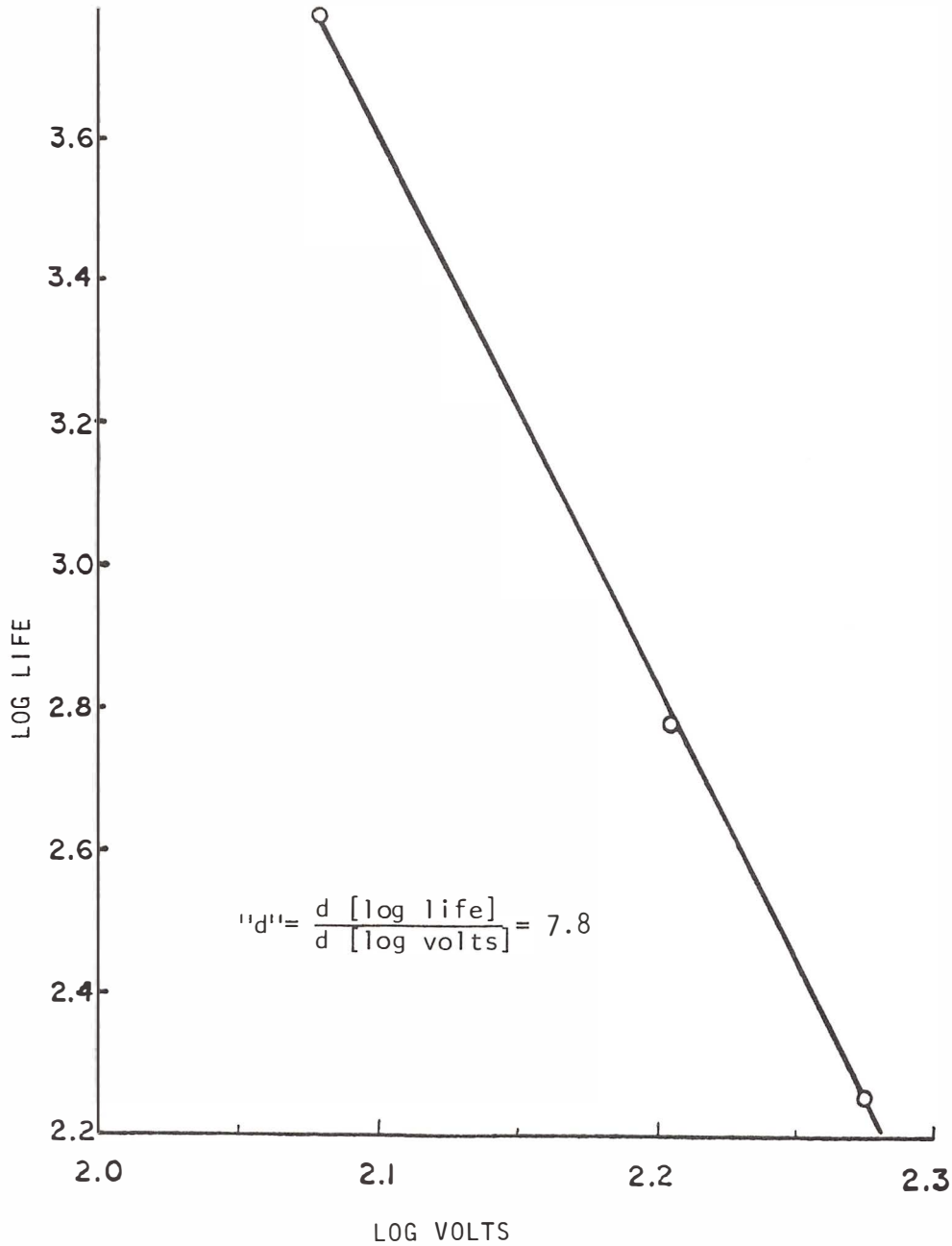


FIGURE 3

IODINE LAMP LIFE AT 7100mm XENON PRESSURE

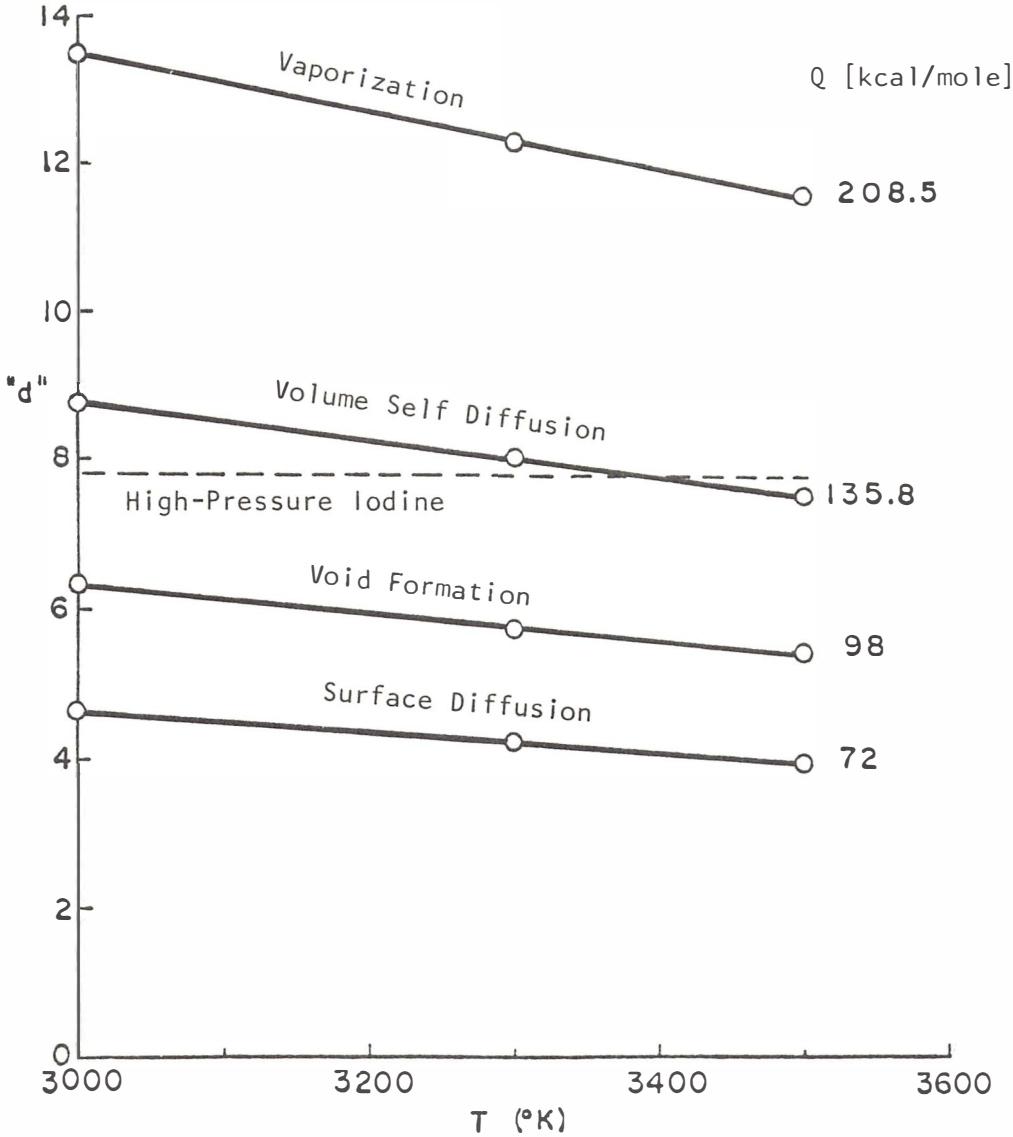


FIGURE 5

CALCULATED AND OBSERVED LIFE EXPONENTS

CONCLUSIONS

1. There seems to be no question but that the burn-out mechanism for high-pressure halogen lamps is entirely different from the mechanism involving evaporation which has been postulated for general service lamps.
2. On the basis of known activation energies, it would seem that the most likely mechanism for burn-out of the high pressure lamps involves the volume self-diffusion of tungsten as the rate determining process.
3. Both surface diffusion and void formation have activation energies which are too low to explain the observed value of "d." There is a possibility, however, that void formation could be responsible for burn-out, but the only way in which this could be true would be the condition that the burn-out mechanism would depend on the four-thirds power of the diameter of the voids.
4. Although the analysis can say nothing about the magnitude of the life of the lamps but only about the temperature or voltage dependence of the life, the observed value of "d" does give one a guide on which to base a detailed theory of the burn-out mechanism.

REFERENCES FOR ADDITIONAL IN-DEPTH INFORMATION

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25.0 TROUBLE SHOOTING HALOGEN LAMP PROBLEMS

25.1 BRITTLE FILAMENTS

In addition to the usual causes of brittle wire in incandescent lamps, the halogen dose can be the problem in halogen cycle lamps.

The reaction of carbon with the tungsten coil can cause the filament to become brittle, resulting in "cold break" during shipping or when the lamp is subjected to mechanical shock. This problem is particularly severe in higher wattage lamps when a high level of bromine is required. If this bromine is introduced into the lamp in the form of CH_2Br_3, an unacceptable amount of carbon is also introduced. As an example, Erlangen was forced to modify the fill gas from CH_2Br_3 to HBr on FCS lamps to eliminate coil breakage.

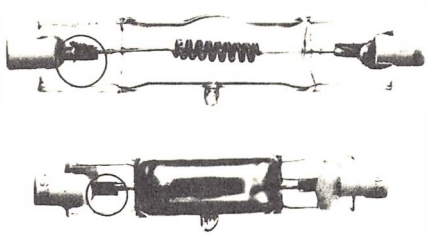
The above problem can often be resolved by using a combination of CH_2Br_2 and HBr; thus retaining some of the advantages of CH_2Br_2.

25.2 BULB DISCOLORATION

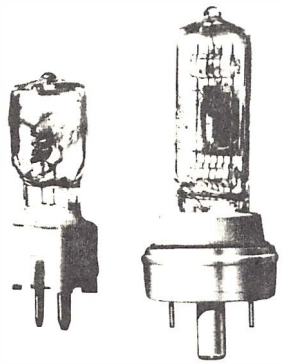
Excess carbon from the decomposition of CH_2Br_2 can cause black spots and streaks. To evaluate a test lamp, bring the coil temperature up slowly to about 1000°C. If excess carbon is evident, adding HBr to dose and decreasing CH_2Br_2 will reduce the problem.

25.3 SEAL FAILURE

The seal failures pictured here could have been caused by inadequate cooling in the equipment or a defect in manufacture. It is advisable to thoroughly check the equipment in which the lamp is operated. If the seal of a tungsten halogen projector lamp fails before the lamp reaches rated life, it usually means the temperature at the seal has been running above its maximum limit. (See Section 23.7 Measurement of Press Seal Temperature.



25.4 DEVITRIFICATION



Devitrification: From the dictionary this means, "to deprive of glossly luster and transparency." If skin oils, acids, oil, etc., come in contact with a quartz bulb a process of crystallization will commence and the bulb will weaken and eventually fail. Furthermore, the area of the bulb affected will change from transparent to transclucent as that area crystallizes.

25.5 LEAKERS

Gross Leaker: Symptomatically similar to a regular projector lamp; milky, cloudy and sometimes multi-colored appearance identifies the condition caused by a leak in the quartz or Vycor envelope.

Slow Leak: It is possible to have a leak effect in a lamp filled above atmosphere pressure even though the fill pressure is still above atmosphere.

It is generally assumed that air enters a lamp due to the outside air pressure being greater than the cold fill pressure of a lamp. Although the mechanism is not entirely clear, a slow leak on one end of a 5 atmosphere cold fill linear lamp will result in filament end attack at the leaking end, even though the cold fill pressure is 3 or 4 atmospheres. The air may enter by replacement. That is the fill gas expands to 10 or more atmosphere when heated and is forced out through a small leak. When the lamp is shut off, the gas contracts out of the leak and a temporary vacuum allows a small amount of air to enter the lamp.

The generally accepted leak mechanism is that gases will diffuse such that the gas mixture in the lamp will tend to become similar to the environment outside the lamp.

25.6 EXCESS HALOGEN ATTACK

It has been known from the beginning that lamps with excess halogen fail early in life. The dose tolerance decreases going from iodine to bromine to chlorine. There is a temperature range for each halogen where the lower temperature is too low for halogen attack and the upper end is above the thermal decomposition temperature of tungsten halide.

Halogen	Attack Range
Iodine	800°C - 1200°C
Bromine	425°C - 1400°C
Chlorine	300°C - 2000°C

The low side of the range is below the temperature at which H_2O cycle, O_2 cycle or CO/CO_2 cycle operate. This means that excess halogen attack will take place much closer to leads or on leads themselves or on supports well away from filament. The high side of the range is the beginning of thermal decomposition temperature. Therefore, the tungsten can and will be redeposited in area of first, second or third filament turn or in same general area as H_2O or oxygen cycle would operate. There will be whiskers and crystal build up but no etched on thin turns in this area as in H_2O or O_2 cycle.

In some cases of excess halogen, the entire filament will become faceted and look like hundreds of tiny mirrors. This is redeposited tungsten from evaporated W from hot part of filament in addition to redeposited W from cooler areas due to halogen attack.

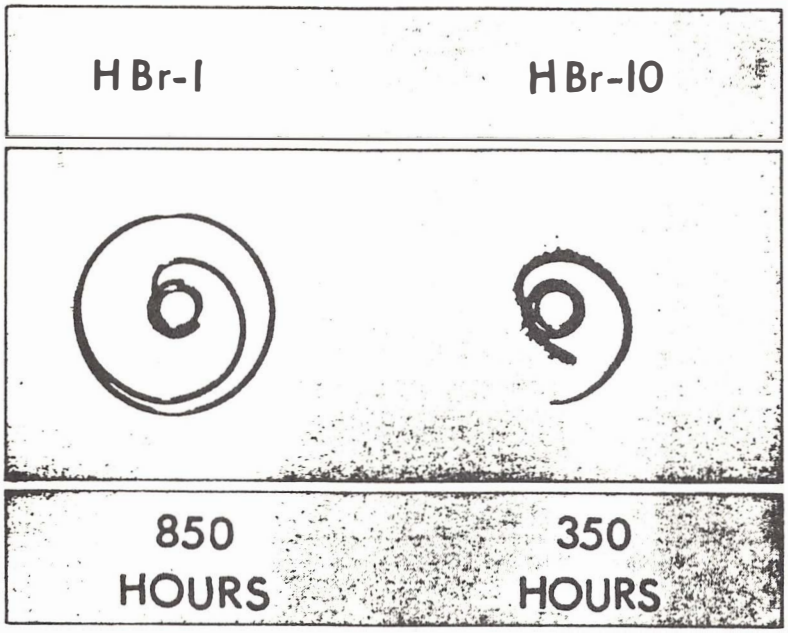


Figure 3

Comparison of attack on lamp supports operated in one and ten torr HBr.

25.7 ARCING

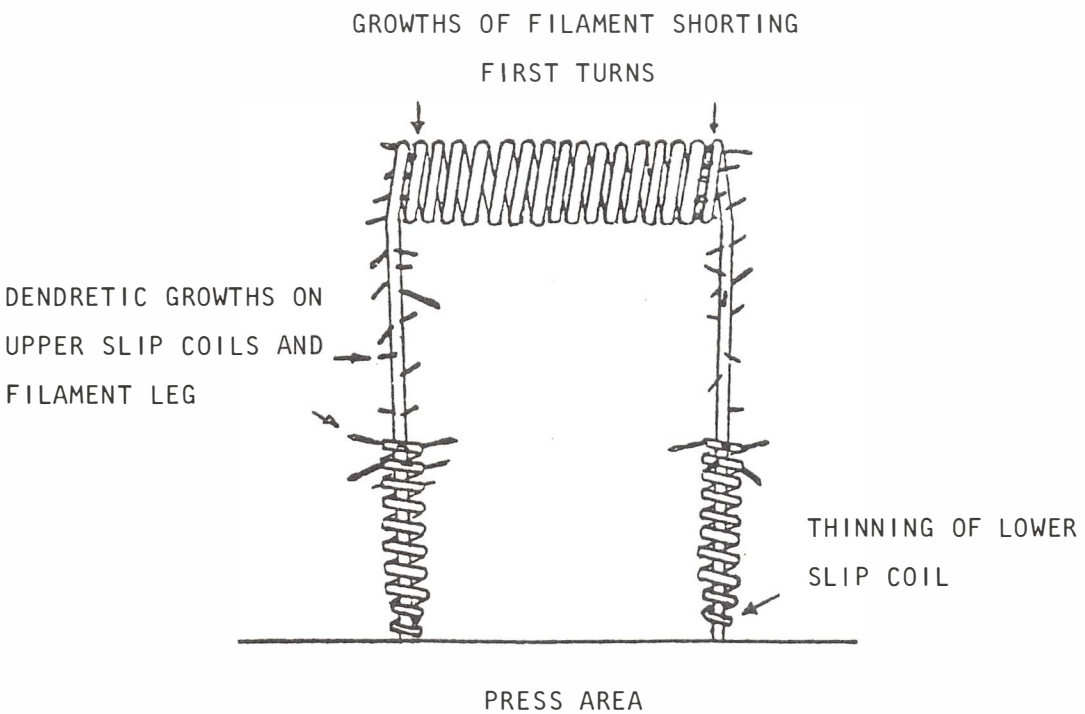
Arcing is the result of fill gas flashover potential, distance between leads, lamp voltage and temperature of filament and leads. Double ended linear lamps do not arc out. High efficiency - single end - small bulbs are most arc prone. 100% Nitrogen is most arc resistant fill and for short life lamps, excess HBr can be added for additional arc resistance. Some lamps have up to 10% HBr in the fill gas.

25.8 LAMP EXPLOSIONS

Bulb Strength

A lamp can explode due to too high an internal pressure. The pressure rise in a lamp is related to the operating temperature and the bulb becomes weaker with rising temperatures.

$$P_1T_2 = P_2T_1$$



EXCESS BROMINE CYCLE ON TUNGSTEN

The pressure rise due to temperature alone is indicated in the following table.

Fill Pressure (cold)	Bulb Temperature °C					
Atmos	300	400	500	600	700	800
4	7.64	8.98	10.31	11.64	12.97	14.31
5.	9.55	11.22	12.88	14.55	16.22	17.88
6	11.64	13.46	15.46	17.46	19.46	21.46
7	13.37	15.70	18.04	20.37	22.70	25.04
8	15.28	17.94	20.61	23.28	25.95	28.61

For common lamps, the operating pressure is about 3 times the fill pressure.

At the end of lamp life there is often an arc sometimes followed by bursting of the lamp envelope. While it is true that the current rises due to the arc, the additional heat is not usually the cause of the lamp envelope failure. It is due to the high current passing through the thin ribbon lead seal. This results in I^2R heating which vaporizes the moly -- raises the pressure internally in the press seal and the whole envelope fails starting at the press.

A somewhat larger moly foil or fusing should be considered for this type of failure.

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